

Experiment

GASES: Dalton's Law of Partial Pressures

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LEARNING OBJECTIVES

The objectives of this experiment are to . . .

- introduce the concept of ideal gases.
- experimentally determine the relationship between pressure and amount of gas, using the *MicroLAB* interface system to collect and analyze the data.
- experimentally determine how the addition of different gases affects Dalton's law, using the *MicroLAB* interface system to collect and analyze the data.

BACKGROUND

One of the major differences between gases and solids or liquids are that the volume of a sample of gas varies when pressure or temperature is changed to a much greater extent than do the volumes of solids and liquids. Solids and liquids are also affected by temperature and pressure, but the magnitude of the volume change is very small. When the densities of solids and liquids are measured, there is little need to control temperature or pressure. Within normal limits of measurement precision, these densities are the same under somewhat different laboratory conditions. As you will observe in this experiment, the density of a sample of gas is much more sensitive to changes in temperature and pressure. The dependence of the density on these two factors is determined by varying the pressure and the temperature separately.

Gases whose liquefaction temperatures are well below room temperature normally act as "ideal" gases. These gases are defined as "ideal" because the attraction between the molecules is negligible in comparison to the kinetic energy of the system and the space between them is large in comparison to the molecular volume, so that the particles act as though they had no attraction or volume.

Pressure is defined as the force per unit area. A gas exerts pressure on any surface it touches. Thus, air, which is a mixture of gases, exerts pressure on the surface of the earth. This pressure is called atmospheric pressure. It depends on the mass of air above the surface and thus will be affected by wind conditions and by the relative elevation of the surface of the earth where the measurement is made with respect to sea level. The *standard atmosphere* (1 atm) is defined as 101.325 kPa. A *pascal* (Pa) is the SI unit of pressure, which is the force of one newton exerted on an area of one square meter.

Atmospheric pressure can support a column of liquid, as shown in Fig. 1. Assume that all three tubes in the figure were originally filled with liquid, then were inverted into the dishes of liquid, as shown. The pressure of the atmosphere on the surface of liquid in each dish, at C and D, is just balanced by the pressure due to the mass of the column of liquid above the surface of the dish, at A, B, and E. If the liquid exerted a greater pressure than the atmosphere, then the level of the liquid would fall until the remaining mass of liquid produced the same pressure as the atmosphere. The same atmospheric pressure is able to support a higher column of liquid 2 than of liquid 1. Since the pressure exerted by the liquid depends on its mass, liquid 2 must be less dense than liquid 1.

Measurement of the height of a column of liquid, supported by a gas, in a tube of uniform diameter, is a convenient way of measuring pressure. The very dense liquid metal, mercury, is usually used to measure pressure. A column of mercury 760.0 mm high exerts a pressure of 1 atm or 101.3 kPa. Laboratory measurements are thus often expressed as cm Hg, or mm of Hg. One mm Hg is also defined as one torr. (After Evangelista Torricelli, the inventor of the barometer used to measure atmospheric pressure.) The density of Hg is 13.6 g/cm^3 and that of the water is 1.00 g/cm^3 . A column of mercury is therefore 13.6 times heavier than a column of water of the same height and diameter, so that the column of mercury will exert a pressure 13.6 times as great as the same column filled with water. A given atmospheric pressure can support a column of water which is 13.6 times as high as the column of mercury. This is one reason mercury is used in barometers and manometers for measuring pressure; a water barometer would have to be 34 feet high!

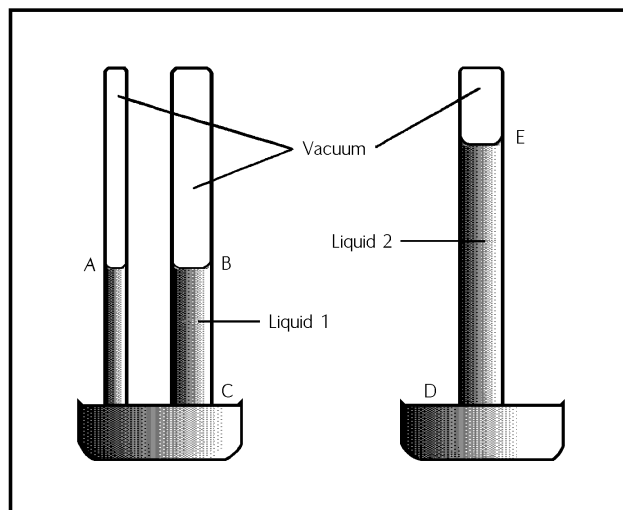


Figure 1. Column of liquid supported by atmospheric pressure.

John Dalton, a British chemist, was one of the first to study the additivity of gases quantitatively. In one set of experiments, Dalton established a relationship between the pressure and amount of a gas. He found that at a constant temperature and volume, the pressure exerted by a gas is directly proportional to the amount of the gas. This relationship has become known as Dalton's Law. Mathematically, this relationship can be stated as follows:

$$P \propto n \quad \text{where "n" represents the amount of gas in moles} \quad (1)$$

The symbol " \propto " means "is proportional to." If we replace the proportionality sign in the previous equation with an equal sign and constant of proportionality, we will obtain another form of Dalton's Law.

$$P = k(n) \quad \text{or} \quad P/n = k \quad (2)$$

We will see how this is derived experimentally in today's experiment.

A second aspect of Dalton's law involves the mixing of different gases. Again, Dalton determined that at constant temperature and volume, the total pressure exerted by a mixture of different gases is directly proportional to the sum of the partial pressures of each gas in the mixture, which in turn, is proportional to the total number of moles of gas present, i.e., to the sum of the number of moles of each gas.

Mathematically, this relationship can be expressed qualitatively as

$$P_T \propto (P_1 + P_2 + P_3 \dots P_n) \quad \text{where } P_T \text{ is total pressure, and } P_n \text{ are partial pressures.} \quad (3)$$

Again, this can be expressed quantitatively as

$$P_T = k(P_1 + P_2 + P_3 \dots P_n), \quad \text{OR} \quad P_T = k \sum_{i=1}^n P_i \quad (4)$$

where k is the constant of proportionality. In words, the total pressure is equal to the sum of the partial pressures. We will see that this proportionality constant is very important in the gas laws.

To accomplish this experiment, we will need to know more about the "ideal gas law." This law is expressed mathematically as

$$PV = nRT \quad (5)$$

where P represents pressure, V represents volume, n represents the amount of gas in moles, R is the gas law constant,

0.08206 L atm/mol K, and T represents the temperature in Kelvin. The most convenient way to transfer a gas is as a certain volume at a given temperature and pressure. For example, in this experiment, we will be withdrawing five ml of gas from a large bag of gas at essentially room temperature and pressure and inject it into an essentially empty flask. Thus, we will need to know how many moles of gas we are transferring in that volume of gas. This can be accomplished by solving the ideal gas law for “n” as:

$$n = PV/RT \quad (6)$$

Avogadro’s law (Amedeo Avogadro, (1776 - 1856), tells us that equal volumes of gas at the same temperature and pressure must contain equal numbers of molecules, or moles of gas. Then if the temperature and pressure of the room remain relatively constant, every five ml addition of gas injected into the flask will contain the same number of moles, or molecules, of gas particles. This is analogous to the way pills are bottled in a modern pharmaceutical plant. Each pill weighs almost identically the same, let us say 1 gram. If the bottle is to contain 100 pills, then the pills should weigh 100 grams. Each bottle is automatically filled with pills until its weight has increased by 100 grams. Similarly, each five ml addition of a gas will add the same number of molecules (or moles or grams) of that gas to the flask. You will need to calculate that number of molecules or that amount of moles from the temperature and pressure at that time.

SAFETY PRECAUTIONS

No chemicals are used in this experiment, so there is no concern for chemical hazards. Eye protection **MUST** be worn in case there is a rupture of the apparatus under pressure

BEFORE PERFORMING THIS EXPERIMENT . . .

...you will need a MicroLAB program capable of
. . . Measuring pressure from an absolute pressure sensor and inputting the corresponding number of moles (which is proportional to the number of mL) from the keyboard. Choose the *press.vs.n.exp* from the **Gas Laws** tab on the opening window.

EXPERIMENTAL PROCEDURE

Equipment set-up

You will use a 60 ml syringe to evacuate the flask and a five ml syringe to measure the volumes of gas added (and hence the number of moles of gas) for this experiment. The equipment will be assembled as shown in Figure 1 using a thick walled 50 ml Erlenmeyer flask, to be used in both parts I and II of the experiment, wrapped in clear plastic tape with a rubber stopper in the top containing a Luer connector. The flask will first be evacuated using the 60 ml syringe, then successive volumes of gas will be added using the 5 ml syringe to measure the effect. You will have available several large gas bags attached to rubber stoppers containing a Luer connector on each, and which will be filled with nitrogen gas for part I of the experiment, and, you will have available several similar large gas bags which will be filled with different gases for part II of the experiment.

Pressure sensor set-up

1. Read the *atmospheric pressure* from the barometer, convert from inches to torr if necessary and record the value in torr as P_{torr} in your lab notes.
2. The *MicroLAB* pressure sensor is factory calibrated, but if your instructor wants you to confirm this calibration, perform steps “a” through “h” as follows, otherwise go to step 3 next.
 - a. Open the *MicroLAB*, select the *press.vs.n.exp* experiment, click on the pressure sensor in the **Data Sources / Variables** view to highlight it, and click **Edit**, then click **Custom Calibration**. Select **Perform a New Calibration**, then **Add Calibration Point**.
 - b. The first calibration point will be with the **Pressure Sensor** open to the atmosphere. Press **Enter** to record your first calibration point.
 - c. To collect the remaining calibration points, use the two and three way valve system detached from Erlenmeyer

flask.

- d. Using the atmospheric pressure determined above and Boyle's Law, calculate the pressure for compressing the 30 ml of gas in the syringe to 20 ml and expanding the 30 ml of gas to 60 ml. Be sure to record these values in your lab notes.
 - e. Adjust the plunger of the syringe to 30 ml volume, attach the Luer lock end to the presser sensor connection on the back of the *MicroLAB*, then close the three way valve of the assembly to form a closed system. **Note:** The volume of the assembly is approximately 5 mL.
 - f. While one student presses the syringe to the 20 ml value and holds it steadily there, a second student should enter the calculated value and press **Enter** to record the volume and pressure.
 - g. Again, while one student pulls the syringe out to the 60 ml value and holds it steadily there, a second student should enter this calculated value and press **Enter** to record the volume and pressure.
 - h. You should now have three points on the calibration screen that lie in a straight line. Select **First Order (Linear)** option to obtain the regression line through the points and the program should have returned you to the **Main Screen**.
 - i. You now have completed the calibration procedure.
3. You will need to set the units for the **Pressure** sensor to torr. Open the *MicroLAB*, if not already open, select the *press.vs.n.exp*, click on the pressure sensor, click **Edit**, then click on **Factory Calibrated "Torr."**
 4. Before starting data collection, you should check that the **Digital Display** reading of the pressure is the same, within a percent or two, as the pressure you determined from the barometer. If it is not, consult with your instructor.

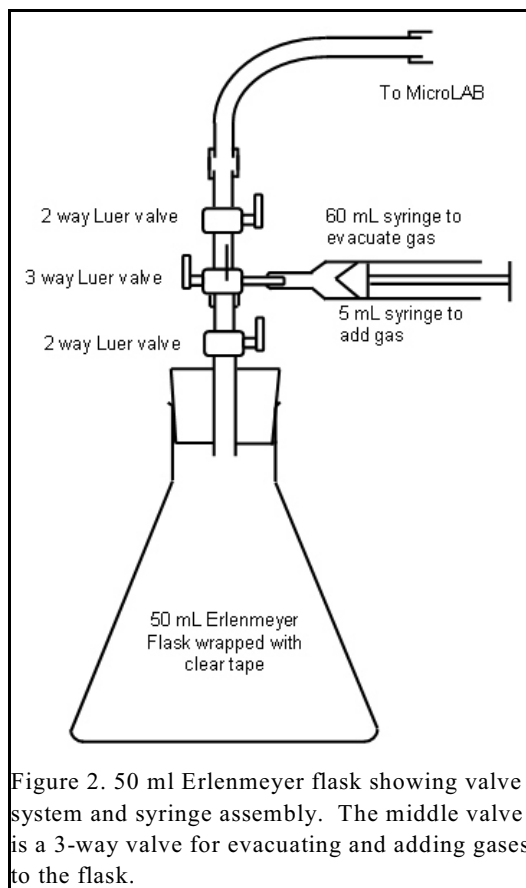


Figure 2. 50 ml Erlenmeyer flask showing valve system and syringe assembly. The middle valve is a 3-way valve for evacuating and adding gases to the flask.

DATA COLLECTION

The effect of additions of the same gas to the total pressure in the container.

(choose a file name for this section of the experiment: _____)

1. **Be sure to use the 50 ml Erlenmeyer flask wrapped in (clear) tape.**
2. With the Erlenmeyer flask attached as shown in Figure 2, and all the valves open, attach the 60 ml syringe to the 3-way valve (the middle valve).
3. Pull the syringe plunger out to the 60 ml position, then close the 3-way valve. This will partially evacuate the system.
4. Make sure the 3-way valve is **CLOSED**, then detach the syringe, push the plunger to the bottom and reattach the syringe to the 3-way valve.
5. Repeat steps 3 and 4 until the *MicroLAB* pressure reading is down to less than 40 torr.
6. Close the 3-way valve and click the **Start** button.
7. Collect data for about 100 seconds in order to determine the leakage rate of the system. This will probably about 3

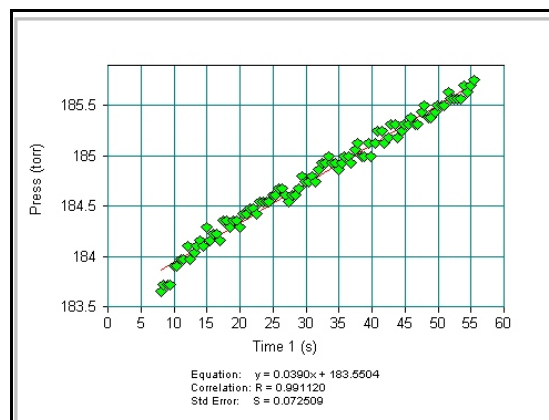


Figure 3. Leakage rate for a fairly tight system. If your leakage rate is considerably faster than this, consult your instructor.

to 5 torr per second as seen in Figure 3.

- Using the 5 ml syringe, withdraw 5 ml of gas into the syringe from the **Nitrogen** filled balloon, detach the syringe, place your finger over the end of the syringe until you can attach the syringe to the 3-way valve. Open the 3-way valve and forcibly inject the gas into the Erlenmeyer assembly by pushing the syringe to the bottom, then close the 3-way valve.
- Enter the total volume added to the Erlenmeyer assembly to that point of the experiment into the **keyboard**, then press **Enter** to record the volume and pressure.
- Repeat steps 5 and 6 as many times as necessary to build the pressure up to around 1200 torr.

The effect of additions of the different gases to the total pressure in the container.

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- Repeat steps 1 through 5 in the above section in order to evacuate the Erlenmeyer flask down to less than 40 torr.
- Repeat steps 6 and 7, drawing gas from the **Nitrogen** filled balloon, at least 6 times.
- Repeat steps 6 and 7 with a minimum of 3 different gases, and preferably at least 5 or more gases so that you can get a reliable slope for the resulting data.
- Be sure that you have a minimum of 15 gas additions, and a minimum of three different gases.

DATA ANALYSIS

The effect of additions of the same gas to the total pressure in the container.

- Using the **Analysis** function, calculate the First Order (Linear) curve fit of the data for the pressure in the flask versus the added volumes, then “click-drag” the function to **Column C** and to the **Y2 Axis**. **Be sure** to record the slope and intercept values in your lab notes.
 - Use the Add Formula button to construct a formula to subtract the initial pressure in the flask from all of the other pressures, i.e., $P - P_0$, then “click-drag” this formula to **Column D**. This will give you the pressure increments between volume additions.
 - Again use the Add Formula button to construct a formula to divide all of the data in **Column D** (i.e., $P - P_0$) by the second value in **Column D**, then change the digits of precision for that column to **0**.
 - Print out this screen as follows:
 - Simultaneously press the **Ctrl** and **Print Screen** keys to capture the **Main Screen** image.
 - Click successively the following sequence: **Start > All Programs > Accessories > WordPad**.
 - With **Wordpad** open, simultaneously press the **Ctrl - V** keys to save the Screen image into **WordPad**.
 - Simultaneously press **Ctrl - P** to print the page. This should print the entire Main Screen for your Dalton’s Law experiment.
 - Use this information to show the validity of Dalton’s law of partial pressures.
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- In your graph, why is the volume of gas added graphed on the *X-axis* and pressure is graphed on the *Y-axis*? Print this graph with the appropriate descriptive title, including your initials.

The effect of additions of different gases to the total pressure in the container.

7. Repeat steps 1 through 4 for the second part of the experiment
 8. Show mathematically how Dalton's Law can be derived from this data.
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9. Does it matter whether the amount of gases added consist of the same gas, or different gases? Explain.

Cleanup

- Dismantle the equipment and return it to the area you obtained it, in at least as good a condition as when you started.
- Be sure to answer the questions on the **Report Sheets**, and follow the instructions given you for completing your lab report.