

Graham's Law of Effusion

The time required for a fixed volume of a number of gases to effuse into a vacuum is measured. These times are proportional to the molecular masses of the gases [1].

MATERIALS

1 or more bags of the following gases: hydrogen (H_2), helium (He), methane (CH_4), oxygen (O_2), and carbon dioxide (CO_2) (See the introduction to this chapter, p. 4, for a description of these bags.) 3-4

drops glycerine

100-mL glass syringe

solid rubber stopper to fit 4-liter filter flask

#10 cork borer (19 mm in diameter)

10-cm length glass tubing, with outside diameter of 19 mm

septum cap to fit 19-mm glass tubing

copper wire, 18 gauge

4-liter filter flask

stand, with clamp to hold flask

vacuum pump, with hose

syringe needle, 27 gauge, cut to a length of ca. 6 mm stopwatch

PROCEDURE

Preparation

Lubricate the syringe with a few drops of glycerine. Bore a hole in the stopper to accommodate the 19-mm tube, and insert the tube through the stopper. Attach a rubber septum to the tube and secure the septum with copper wire. Seat the stopper in the mouth of the 4-liter filter flask and clamp the flask to the stand. Use vacuum hose to connect the tubulation of the flask to the vacuum pump.

Presentation

Turn on the vacuum pump and evacuate the flask. Attach the needle to the syringe and fill the syringe with 100 mL of air. Carefully insert the needle of the syringe through the rubber septum, as shown in Figure 1. (The 27-gauge needle is very fragile and easily bent.) Use a stopwatch to measure how long it takes for 90 mL of air to effuse through the needle into the evacuated flask.

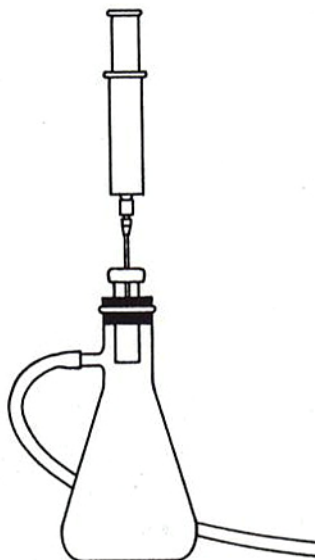


Figure 1

Repeat the process with 100-mL samples of other gases. Prepare these samples by inserting the syringe needle through the septum of each of the bags of gas and drawing 100 mL of gas into the syringe.

HAZARDS

The filter flask is subject to implosion when evacuated. Therefore, it should be wrapped with netting or tape.

Corrosive or toxic gases should not be used, because they will be released into the room after passing through the vacuum pump.

Syringe needles are sharp and potential sources of puncture wounds.

DISCUSSION

Two distinct laws of gas behavior were advanced by Thomas Graham (1806-1869). Graham's law of diffusion was published in 1833, and his law of effusion was published 13 years later. Diffusion occurs when two gases mix without a pressure differential. Effusion occurs when a gas escapes through a small hole in a thin-walled container into a vacuum. This demonstration involves effusion rather than diffusion.

The table lists typical effusion times for 90 mL of various gases. Also listed are

Effusion Times of Various Gases [1]

Gas	t (sec)	t ² (sec ²)	Molar mass (g/mole)
H ₂	7.2	52	2.0
He	11.2	125	4.0
air	21.7	471	29.0
O ₂	22.5	506	32.0
CO ₂	26.2	686	44.0

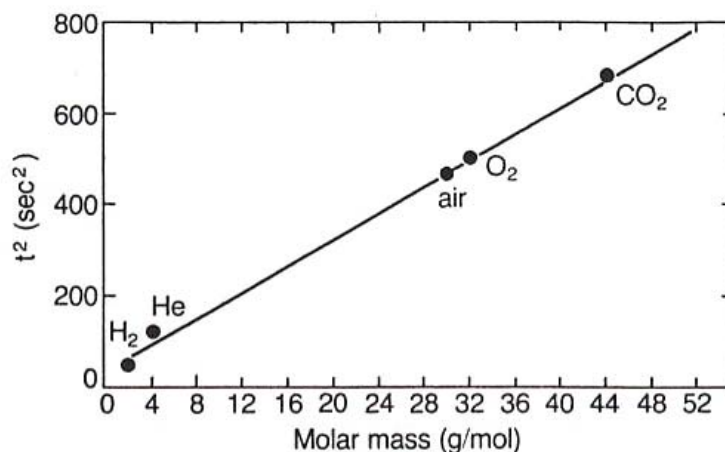


Figure 2. Plot of t^2 versus molar mass.

the squares of the effusion times and the molecular masses of the gases. In Figure 2, the square of the effusion time is plotted versus the molar mass of the gases. This shows that the square of the effusion time is proportional to the molar mass. It follows then that the effusion time is proportional to the square root of the molar mass. Because the effusion time is inversely proportional to the rate of effusion, the rate of effusion is inversely proportional to the square root of the molar mass of the gas.

If the flow of a gas is to be defined as effusion, at least three criteria must be satisfied [2]. First, the average distance a molecule travels between collisions must be at least ten times the radius of the hole through which the gas is flowing. Second, the pressure of the gas must be small enough that a molecule collides with the walls of the container more frequently than with other molecules. Therefore, each molecule escapes from the container independently of any other, and there is no bulk flow of gas through the hole. Third, the thickness of the wall of the container must be a small fraction of the diameter of the container, so that each molecule that enters the hole will succeed in escaping from the container. Although the procedure employed in this demonstration does not strictly meet all of these criteria, the results are in excellent agreement with Graham's law of effusion, which states that the rate of effusion of a gas is inversely proportional to its molar mass. If a longer needle is used, the third criterion will be violated more significantly, and the results of the demonstration will not be in such close agreement with Graham's law.

REFERENCES

1. D. A. Davenport, *J. Chem. Educ.* 39:252 (1962).
2. W. J. Deal, *J. Chem. Educ.* 45:676 (1975).