# EXPERIMENT 2: LOW-PRESSURE EFFUSION OF GASES

Introduction

The purpose of this experiment is to study the flow of gases through small orifices. The flow rates are directly related to the distribution of molecular velocities in a gases, *i.e.* the well-known Maxwellian distribution. An introduction to the kinetic theory of transport phenomena and specifically effusion of gases is given in Shoemaker *et al.*, pp. 117–119. For a general discussion of the Maxwellian distribution, consult a physical chemistry textbook. The flow of gases is a function of molecular weight and temperature. This phenomenon has a practical application in the separation of isotopes. We will follow the rate of effusion of gases through a small pinhole by measuring the pressure drop on the high-pressure side of the pinhole. Relative rates of effusion of several gases (choose three from He, $N_2$, Ar, $CO_2$, and $SF_6$) will be examined. We will be following the procedure given in Experiment 6 of the 3rd edition of the textbook (appended to this write-up).

Theory

In the case where the pressure on one side of the pinhole is much lower than on the other, Eq. (7) on p. 119 of Shoemaker *et al.* can be written as

$$-dN/dt = Ap/(2\pi MRT)^{1/2}, \qquad (1)$$

where $N$ is the number of gas molecules in the reservoir (glass bulb in our case). The pressure drop in the bulb is related to the change in the number of gas molecules in the bulb by the ideal gas law:

$$dN = (V/RT)dp, \qquad (2)$$

Rearranging and defining collected constants as a "relaxation time" $\tau$ gives

$$dp/p = -(A/V)(RT/2\pi M)^{1/2}\,dt = -d\tau/\tau. \qquad (3)$$

Integration of Eq. (3) gives an equation in the form you will use for data analysis:

$$\ln(p/p_0) = -t/\tau. \qquad (4)$$

Experimental Procedure

The vacuum manifold is shown schematically in Fig. 1. The system is pumped by an internally-baffled, metal diffusion pump with integral gate valve. (For a thorough discussion of vacuum techniques, see Chap. XIX of Shoemaker *et al.*, especially pp. 623–628 on mechanical and diffusion pumps.) Before the lab, the vacuum system will be pumped down and ready for operation. The pressure in the bulb will be monitored with a capacitance manometer. In contrast to a McLeod gauge, continuous readings can be made with a capacitance manometer. (Read Shoemaker *et al.*, pp. 630–635.)

**Caution:** The diffusion pump will be damaged if exposed to atmospheric pressure while how. Before starting the experiment, be sure you understand the arrangement of the

You need several apparatus constants to do your calculations. The diameter of the pinhole will be provided by the T. A. Different pinhole sizes will be used in different lab periods. Measure the diameter of the bulb and the length of the copper tubing on the high-pressure side; the copper tubing is 1/4 outside, 1/32 wall thickness. Calculate the volume occupied by the gas on the high-pressure side.

Data Analysis and Discussion

What type of plot is appropriate for logarithmic decay? Should the points in such a plot be equally weighted? How is the size of the error bars determined? How do the errors in $\tau$ propagate to your calculated molecular or atomic weights? A table of data and determined values of $\tau$ should be presented. Compare the ratios of the decay constants for the different gases from the theoretically expected ratios.

The pinhole diameters in our apparatus are comparable to the thicknesses of the plates in which they have been drilled. Thus, our pinholes are more like channels rather than orifices. The flow out of a channel of a given inside diameter is less than for flow through an orifice of the same diameter. What effect will this have on your calculated atomic or molecular weights? What do you consider to be the major sources of error in determining the absolute values of the molecular weights in this way? Do a calculation to determine the fractional enrichment of the isotopic molecules $^{238}UF_6$ and $^{235}UF_6$ in a mixture of the two species after a certain fraction of the gas has passed through a pinhole. What might one do to get a 10 % enrichment?

taken from a previous edition of the textbook [D. P. Shoemaker, C. W. Garland, and J. I. Steinfeld. *Experiments in Physical Chemistry*, 3rd ed.].

## EXPERIMENT 6. LOW-PRESSURE EFFUSION OF GASES

In Exp. 4 we were concerned with the viscous flow of gas through a capillary tube. One of the conditions for that experiment was that the mean free path of the gas must be small compared with the diameter of the tube. Actually, the flow ceases to be purely viscous and begins to assume some molecular character when the slip correction



becomes significant. When the mean free path becomes very large in comparison with the diameter of a tube or hole, the flow is completely molecular in character.

At a given temperature, the mean free path $\bar{\ell}$ is inversely proportional to the pressure; for most gases, $\bar{\ell}$ is of the order of $10^{-5}$ cm at 1 atm and about 0.05 cm at a pressure 0.1 Torr (see Table IV-1). Clearly, it is difficult to obtain the necessary conditions for molecular flow at 1 atm pressure, since extremely small holes or pores are needed. Demonstrations of molecular flow at 1 atm with pinholes punched in foils are of no value, although they may appear to give correct flow time ratios for two gases if the choice of a pair of gases for study is fortuitously such that the molecular diameters are about the same. In general the results of such experiments show a dependence of flow time on molecular diameter, which is a property of viscous flow and not true of pure molecular flow. Valid molecular flow can be achieved, however, using holes with diameters of about 0.01 cm if the gas pressure is 0.10 Torr or less.[1] Such low-pressure effusion of helium, argon, and carbon dioxide will be studied in this experiment.

### METHOD AND THEORY

Effusion will be studied for gas at low pressure flowing through a small pinhole into a vacuum. The experimental apparatus is shown in Fig. 1. The important features of this apparatus are: (1) a system for obtaining high vacuum; (2) a large bulb $B$ (about 5 liters), to contain the gas to be studied, at an initial pressure of 0.1 to 0.2 Torr; (3) an orifice $O$ in the form of a pinhole of the order of 0.1 mm in diameter in very thin platinum foil, through which the gas in bulb $B$ may effuse into the high-vacuum part of the system; (4) a vacuum gauge for measuring periodically the pressure of the gas remaining in bulb $B$; and (5) an expansion system for filling bulb $B$ with gas at the desired initial pressure.

For this method we can write Eq. (IV-7) as

$$-\frac{dN}{dt} = \frac{Ap}{\sqrt{2\pi MRT}} \tag{1}$$

where $N$ is the number of moles of gas in the bulb $B$ at pressure $p$ and temperature $T$, $A$ is the area of the pinhole, and $M$ is the molecular weight of the gas. In Eq. (1) we have made use of the fact that the pressure outside the pinhole is essentially zero ($10^{-5}$ Torr or less). Applying the perfect-gas law to the gas in the bulb $B$ (volume $V$) we write

$$dN = \frac{V}{RT}\,dp \tag{2}$$

Combining Eqs. (1) and (2) gives

$$\frac{dp}{p} = -\frac{A}{V}\sqrt{\frac{RT}{2\pi M}}\,dt = -\frac{dt}{\tau} \tag{3}$$

where $\tau$ is the "relaxation time" for the system and is

$$\tau = \frac{V}{A}\sqrt{\frac{2\pi M}{RT}} \tag{4}$$

For a given apparatus and choice of gas, $\tau$ is a constant if $T$ does not vary; therefore, Eq. (3) can be integrated to give

$$\ln\frac{p}{p_0} = -\frac{1}{\tau}t$$

or

$$\log p = \log p_0 - \frac{t}{2.303\tau} \tag{5}$$

where $p$ is the pressure in bulb $B$ at time $t$ and $p_0$ is the initial pressure (at $t = 0$).

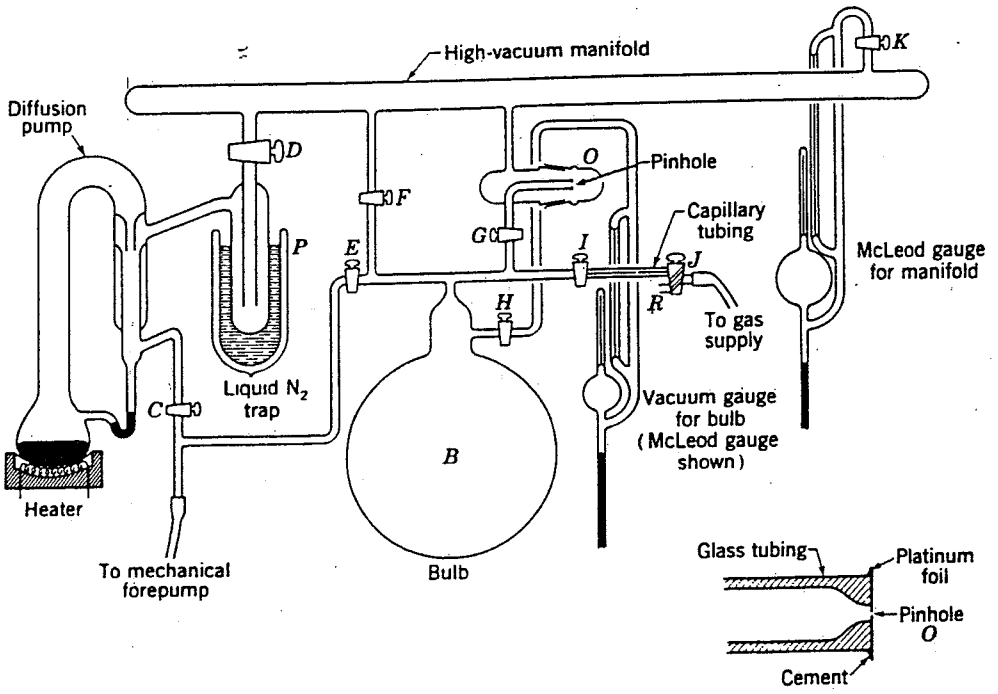


FIGURE 1
Apparatus for the low-pressure effusion of gases.

A plot of log $p$ versus $t$ should be a straight line. From the slope we can evaluate $\tau$ and then use Eq. (4) with known values of $A$, $V$, and $T$ to calculate the molecular weight of the gas. Even if we do not know the value of $A/V$, if we obtain data for two different gases, we can determine the ratio of their molecular weights.

## EXPERIMENTAL

Before the run is started, the entire system should be evacuated to a pressure of $10^{-5}$ Torr or less and liquid nitrogen should be placed in the Dewar flask around trap $P$. Either this will be done by an instructor before the period, or instructions will be issued for the proper procedure to be used. The pressure should be checked with the McLeod gauge which connects to the manifold through stopcock $K$. For a general discussion of high-vacuum systems and components see Chap. XVII.

The actual apparatus may differ from that shown in Fig. 1, in which case special operating instructions will be available. The procedure given here will refer to the system shown. When the system is completely evacuated, all stopcocks will be open except $E$ and $J$.

The pressure gauge which is connected to the bulb by stopcock $H$ will be either a small-volume McLeod gauge or a thermocouple gauge. If it is a McLeod gauge, readings during the run should be taken as quickly as possible, since a small amount of gas is cut off in the gauge during a pressure reading. If the gauge is a thermocouple gauge, this precaution is not necessary but the gauge must be calibrated against the manifold McLeod gauge with each gas used. This calibration can be done after the run by the following procedure: Close $D$ and $E$; open $H$, $F$, and $K$; admit gas to the entire line at the highest required pressure through $J$ and $I$. Now read both the McLeod and the thermocouple gauge. Reduce the pressure by opening $D$ momentarily and repeat the measurements; continue until the desired range has been covered, and plot a calibration curve. (For precise calibration at very low pressures, one can insert a cold trap between the manifold and the McLeod gauge to eliminate mercury vapor.) A discussion of the thermocouple gauge is given in Chap. XVII.

**Procedure** Connect the gas inlet hose to a cylinder of helium, argon, or carbon dioxide which has a regulator valve, and adjust the pressure to about 2 psi above 1 atm. Carefully turn stopcock $J$ so that the hose can be flushed out through outlet $R$ of this stopcock. Close stopcock $I$ and turn $J$ so as to fill the short length of capillary tubing with the gas. Now close $J$, $F$, and $G$, and open $I$ to allow the slug of gas to expand into the bulb $B$ and its associated pressure gauge. Close $I$ and measure the pressure in bulb $B$. If the pressure is between 100 to 150 $\mu$m (micrometers) (0.10 to 0.15 Torr), the run can be started; if above 150 $\mu$m, open stopcock $E$ *momentarily* to reduce the pressure to the range 100 to 150 $\mu$m.

To start the effusion, open stopcock $G$ which connects the bulb $B$ to the high-vacuum manifold through the pinhole at $O$. Take pressure readings on the gas in $B$ at 5-min intervals. Continue readings until the pressure is down to about 5 percent of its initial value. Record the ambient temperature near bulb $B$. At least once during the run, check the manifold pressure (with the McLeod gauge at $K$) to verify that it is less than $10^{-4}$ Torr. Except for this measurement, keep stopcock $K$ closed during the run.

To terminate a run, open $F$ and $I$ to allow the diffusion pump to evacuate the system to a high vacuum.

Repeat this procedure with one or both of the other gases. When this experiment has been completed, leave the apparatus evacuated unless otherwise instructed.

Record the necessary apparatus constants $A$ and $V$.

## CALCULATIONS

Convert all pressure-gauge readings obtained during a run to micrometers of mercury ($p$) and plot $\log p$ against the time in *seconds*. Alternatively, if a McLeod gauge was used, one can simplify the calculation by plotting $2 \log h$ versus $t$, since the pressure is proportional to $h^2$, where $h$ is the gauge reading.

From each plot, determine $\tau$ from the slope and $p_0$ from the intercept at $t = 0$. Compare this $p_0$ value with the pressure prior to opening stopcock $G$. Using Eq. (4) compute the molecular weight $M$ for each gas studied. Also compute the ratio of molecular weights from the ratio of $\tau$ values. The agreement with accepted values is expected to be better for the ratio than for the individual values because the effect of uncertainties in $A$ and $V$ has been eliminated.

## DISCUSSION

Calculate the mean free path of each gas at pressure $p_0$. How does this compare with the pinhole diameter?

Estimate the effect of neglecting the back effusion from the manifold into the bulb.

For the highest effusion rates attained in this experiment, what is the minimum pumping speed required for the vacuum system to maintain a manifold pressure no higher than $10^{-4}$ Torr?

An alternative method employs effusion through a pinhole from one bulb to another of equal volume. How would you define a relaxation time $\tau'$ for this method, and what relationship would $\tau'$ bear to $\tau$?

Suggest how an effusion experiment could be designed and carried out to measure a very low vapor pressure for a solid.

## APPARATUS

High-vacuum system; effusion apparatus such as that shown in Fig. 1; heavy-wall rubber tubing; stopwatch; Dewar flask for cold trap.

Cylinders of helium, argon, and carbon dioxide; stopcock grease; liquid nitrogen (1 liter).

## REFERENCE

1. M. Knudsen, *Ann. Physik*, **28**, 75 (1909).

## GENERAL READING

E. H. Kennard, "Kinetic Theory of Gases," McGraw-Hill, New York (1938).

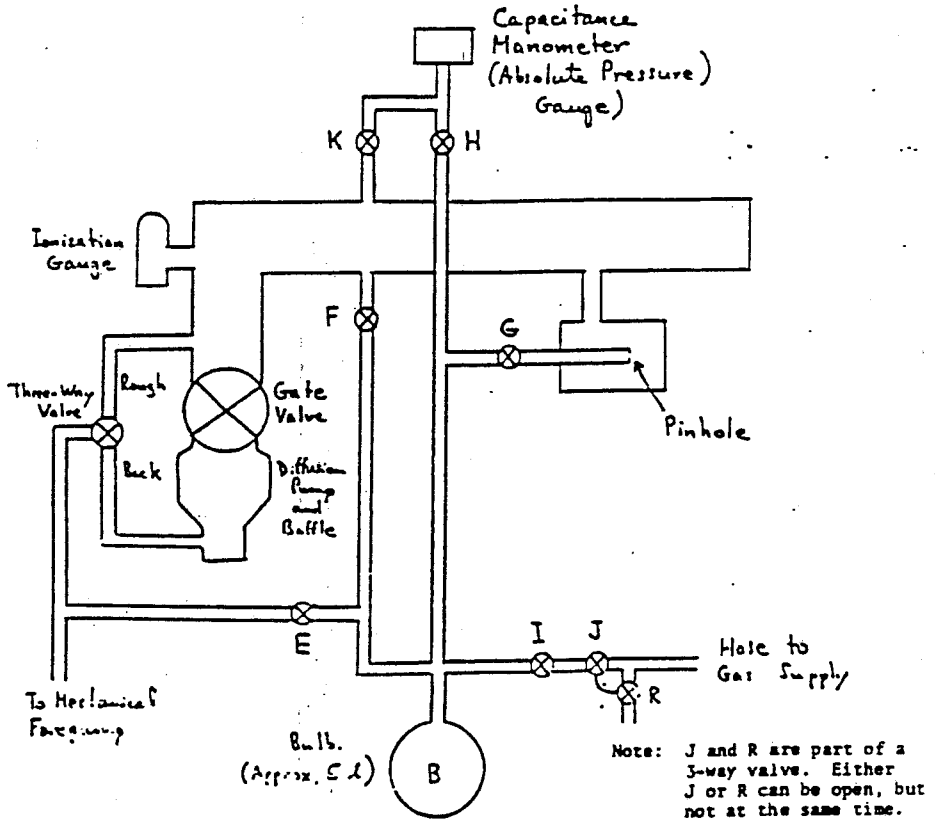


Figure 1. Schematic of the vacuum manifold.

apparatus and are familiar with the detailed procedure below. The T. A. will check your knowledge before you can begin the experiment.

Detailed Procedure

Connect the gas supply hose to a gas cylinder which has a regulator valve, and adjust the pressure to about 2 psi above 1 atm. Keep outlet *R* open for several minutes to flush out the hose, then close *R*. Close valve *I* and open *J* momentarily to fill the short section of tubing with gas. *Under no circumstances should valves I and J be open at the same time.* With *J* reclosed, now close valves *K*, *G*, and *F* and open *I* to allow he slug of gas to expand into bulb *B*. If the pressure is above 0.15 Torr, *momentarily* open valve *E* to reduce the pressure. A run can be started between 0.1 and 0.15 Torr.

Open valve *G* to start the effusion. (Notice the ionization gauge pressure at the low-pressure side of the pinhole.) Take pressure readings in the bulb (capacitance manometer) at 2–5 min intervals, and continue until the pressure is down to about 5 % of its initial value. Record the ambient temperature. To terminate a run, open valves *F*, *I*, and *K* to evacuate the system to high vacuum.

Do several runs with helium and two other gases. From the length of the first run, can you predict how long a run with the other gases will take?