

LOW PRESSURE EFFUSION OF GASES

This experiment will introduce you to the kinetic properties of low-pressure gases. You will make observations on the rates with which selected gases and gas mixtures effuse through a pinhole with a diameter that is smaller than the mean free path of the gas molecules. You will analyze your results in terms of the kinetic theory of gases.

1. Introduction

Consider the following system. A gas is confined in a vessel having a small orifice in one wall and a good vacuum outside that wall. Question: What characteristics of the system govern the rate at which gas flows through the orifice? Obviously at least two parameters are of importance, the gas pressure within the system and the orifice size. Two general conditions may apply.

In the first case, let us say the gas pressure is high, one atmosphere or higher. Under these conditions the mean free path, defined as the average distance traveled by molecules between collisions, will be small. At one atmosphere and 25° C the mean free path is about 10^{-5} mm. Because the mean free path is small, collisions between molecules are far more frequent than collisions between molecules and the wall. The gas will act as a continuous medium rather than as a collection of individual molecules; the flow can be described and analyzed hydrodynamically. The coefficient of viscosity will appear in equations describing such flow.

In the second case, let the gas pressure be low, a few tens of microns (1 micron = 10^{-3} torr, 1 torr = 1 mm Hg). Under these conditions the mean free path will be the order of 1 mm or larger, and the rate of collisions with walls will approach the rate of molecule-molecule collisions. Under such conditions, the gas can be considered to be composed of individual molecules rather than a continuous medium. The term molecular flow applies in this case. The rate of flow through the orifice will be governed by the collision frequency with the wall and the dimensions of the orifice. We can describe this rate of flow using models derived from the kinetic theory of gases.

Your objective in this experiment will be to test the predictions of kinetic theory for a simple (ideal) model of gases and gas mixtures.

2. The Kinetic Theory of Gases and a Model for Effusion

We know that the molecules of a gas are constantly undergoing collisions, with each other and with the walls of the vessel containing them. The properties of the gas are governed by the

characteristics of these collisions. One way we can characterize the collisions in our gas sample is with reference to the velocity distribution function:

$$\frac{dn}{N} = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} c^2 e^{-mc^2/2kT} dc \quad (2)$$

where dn/N gives the fraction of molecules moving with speeds between c and $c+dc$. Note that this distribution function depends only on the mass m of the gas atom (or molecule) and the temperature. Distribution functions are useful for computing averages, and thus we can find, by averaging c for example, that the average speed in a gas of molecular mass m and temperature T is:

$$\langle c \rangle = \left(\frac{8kT}{\pi m}\right)^{1/2} \quad (3)$$

In this experiment we will be concerned with the rate at which atoms and molecules of specified mass effuse at low pressures through a pinhole. To interpret our observations we will need a model for this process. To construct such a model let us consider first the more general problem of the collision frequency per unit area of a gas with a surface. This collision frequency is regulated by the velocities in our sample: the number of collisions per second per unit area of surface involving gas particles with velocity c is just the product of that velocity with the density of those particles. Of course we have many velocities in our sample, and to find the overall collision frequency we need to consider them all, weighted by their relative magnitudes in the velocity distribution function. Integrating over all velocities and pertinent directions a collision frequency per unit area can be expressed in terms of the average velocity,

$$\Gamma_n = \frac{1}{4} n \langle c \rangle \quad (4)$$

$$\Gamma_n = \left(\frac{kT}{2\pi m}\right)^{1/2} n \quad (5)$$

where n is the density in molecules per unit volume. Converting to molar units, we can write:

$$\Gamma_{N/V} = \left(\frac{RT}{2\pi M}\right)^{1/2} \frac{N}{V} \quad (6)$$

which, using the ideal gas equation, can be expressed as:

$$\Gamma_P = \frac{P}{\sqrt{2\pi MRT}} \quad (7)$$

Now let us consider a section of wall, of area A , comprising an orifice. Gas molecules striking this portion of surface exit the vessel by effusion. If we can assume that back effusion is negligible (i.e., a good vacuum exists on the outer side of the wall), then the total effusive flux is

simply the flux per unit area striking the surface, Γ_P times the area of the orifice, A . In terms of moles of gas lost per unit time:

$$\frac{dN}{dt} = \frac{-AP}{\sqrt{2\pi MRT}} \quad (8)$$

Because pressure is the variable we will be monitoring, it will be useful to change variables from (extensive) moles to (intensive) pressure, for which we will need to consider the volume of our system. Substituting for N from the ideal gas equation of state $dN=V/RT dP$, Eq. (6) rearranges to:

$$\frac{dP}{P} = -\frac{A}{V} \left(\frac{RT}{2\pi M} \right)^{1/2} \cdot dt \quad (9)$$

$$= -Cdt \quad (10)$$

This expression is easily integrated to yield an exponential expression for the instantaneous pressure as a function of time:

$$P = P_0 e^{-Ct} \quad (11)$$

where the constant C depends upon the volume of the apparatus, the temperature, the size of the pinhole and the molecular weight of the gas.

In the present experiment you will investigate the effusive properties of He and N₂. You will verify their conformance with the ideal gas equation of state, and from a quantitative analysis of their behavior, you will calibrate the orifice size and volume of your apparatus. You will then study the effusion of a mixture of He and N₂, rationalizing your observations by constructing a simple model for your system.

3. Simulations Using the Diatomic Molecular Simulation Program

Use of the simulation program on the computers in the terminal room will give a better idea of the effect of the Maxwell-Boltzmann distribution function, Eq. 2, on the effusion rates which will be monitored in this experiment.

To start the program double click on the Diatomic icon, then start. Open the Statistical Mechanics window and click on the "Translation" tab. Select "Speed Distribution" from the plot menu. Set the middle temperature dial to 300 K and the others to 0K. Choose N₂ as the molecule. What is the most probable speed for a nitrogen molecule at 300K? This is the speed at the peak of the curve. Click on the curve to see a readout of the x- and y-coordinates of the mouse. Find the speed at the top of the curve. Note that

the speeds are in kilometers per second. Multiply by about 2200 to get the speed in miles per hour. Increase the first temperature dial from 0K to 100K. How does this curve compare to the 300K curve? Does a three-fold increase in temperature produce a three-fold increase in the most probable speed? Use the third dial to plot a curve at 1000K.

Print this plot if the three speed distributions at 100, 300, and 1000K.

Return all temperature dials to 0K except the 300K one. Change the molecule to H₂ and I₂. How do the plots change when the molecule changes? What trend is observed? Look carefully at the speed axis (the x-axis).

Include the plot above in your laboratory report along with the answers to the above questions.

4. Lab Report

Your lab report should include the following:

1. Prepare four plots, two showing data for He runs and two for N₂ runs. Plot your data in two ways on each plot, as pressure vs. time (left-axis) and $\ln[P/P_0]$ vs. time (right-axis). Include these graphs with the corresponding tables of raw data.
2. Make a table listing the following parameters as they pertain to, or are derived from each run; run number, gas, relaxation constant (C), calculated value of the pinhole size, A (your system volume, V, will be given in lab).
3. During the second week you will measure the relaxation constant for an unknown gas. The fact that the relaxation constant varies as the inverse square root of the mass will

allow you to determine the molecular weight of the unknown gas, and hence to identify it. Specifically, $M_u = 28[C_{N_2}/C_u]^2 = 2[C_{He}/C_u]^2$, where C_{N_2} and C_{He} are the relaxation constants for N_2 and He, respectively. You must use error propagation to determine the uncertainty of your mass determination for the unknown gas from the uncertainties of the relaxation constants. You should calculate the mass of the unknown gas from the relaxation constants of both He and N_2 and compare the results. In principle, the values should agree within the uncertainty of the measurement. Do they?

4. In your conclusions, consider in light of your data, the accuracy of the simple equation we derived for the rate of effusion from the kinetic theory of ideal gases. Comment on the consistency of your observations on each gas from run to run, and between He and N_2 . Which runs were better for each gas? Why? What is the diameter range of the pinhole as estimated from your data for He and N_2 ? From the mass and uncertainty that you determined for the unknown gas, indicate how certain you are of the identify of the unknown gas.

5. Lab Report Questions

1. The simple exponential decrease of pressure with time predicted by the kinetic theory of gases can be characterized by either the relaxation constant C , or by a half-life, $t_{1/2}$. The half-life is the time it takes for the pressure to decrease to one half of its initial pressure. What is the relationship between C and $t_{1/2}$? Does the half-life you calculate from a measured relaxation constant agree with the half-life read directly from your plots of P vs. t ? Is the time it takes for the pressure to fall to $1/4$ of its initial value simply twice the half-life? Explain.
2. Based on the area of the pinhole that you have determined, comment on whether the key assumption in using the kinetic theory of gases to derive the effusion rate is valid. Obviously, you have to know what this assumption is.
3. Is there any reason the experiment might not work as well for a heavy gas as for a light gas?
4. From your results, comment on the advantages and disadvantages of determining the molecular weight of a pure gaseous substance by gas effusion as compared with mass spectrometry.

EXPERIMENTAL PROCEDURE

The Apparatus

A diagram of the apparatus used in this experiment is attached. The apparatus uses two types of valves, two types of vacuum gauges, and two types of pumps. The first type of valve is the butterfly valve, which opens and shuts with only a 90 ° turn; turn clockwise to shut, counterclockwise to open. The slot in the knob indicates whether the valve is in the opened or closed position. There are three butterfly valves on the system. The second valve type is the bellows-sealed valve. These take several 360 ° turns to open and close; they also open by turning counterclockwise and shut by turning clockwise. Both types of valves are delicate and should be handled with care. The bellows valves should not be opened all the way but should be left with about a 10 ° turn from fully open. There is one baratron vacuum gauge and three thermocouple gauges on the system. Most of your measurements will be made with the TC gauge on top of the system, TC1. The TC gauges have a range of 2000 microns to 1 micron. For pressures less than 1 micron the gauges read 0 or even negative numbers. When negative readings are observed they indicate that the gauge controller has not been zeroed properly. The baratron gauge can be used for pressures from 1 atm (about 7.6×10^5 microns) to 1000 microns. The thermocouple gauge should not be left on for long periods when the pressure is above 2000 microns. The system is pumped by a rotary mechanical pump (MP) and a diffusion pump (DP). The MP can be used from atmosphere down to its limiting pressure of 1-10 microns. In contrast, the DP can only be used when the pressure is below about 200 microns. The DP achieves low pressures by heating a high molecular weight oil. This oil will oxidize if exposed to pressures above 200 microns while hot. The outlet of the DP is pumped by the mechanical pump through valve A.

Initial Pump Down of the Vacuum System

During the semester, the apparatus should be left under vacuum. However, if you need to pump down the entire system from atmosphere, use the following procedure. This procedure presumes that the DP is cold and that the entire system is at atmosphere. If only the gas manifold is at high pressure and the pumping station is under vacuum, use the second procedure described below.

1. Make sure the gas inlet valve (valve G), and the gas cylinder valves are closed. Open the following valves: all three butterfly valves (A, B, and C), the pinhole valve (valve D), and manifold valves E and F.
2. Plug in the mechanical pump. It should start pumping and will initially make some gurgling sounds but then should quiet down in a minute or two. After three to five minutes, the pressure should be low enough to read with the thermocouple gauge. In about 10 minutes, it should read below 10 microns. The baratron gauge can be used to read the pressure from atmosphere to 2000 microns.
3. Make sure water is flowing through the DP cooling coils. Close valve C, then plug in the diffusion pump. As the oil begins to heat it gives off gases (this is known as outgassing) and

the pressure may rise initially. After a few minutes, the pressure should fall. It should eventually fall to a lower value than was achieved with the mechanical pump alone and should be lower than can be read by the TC gauge, i.e., it should read 0 or slightly negative.

4. Test to see if the pressure rises when there is no pumping by closing valve B. If the pressure rises by more than 1 micron in 10 seconds, the system may either have a leak or there may still be some outgassing from the walls. To check for the latter possibility, let the system pump for another 15 minutes by opening valve B again. Does the pressure then stay constant after valve B is closed? If not, there may be a small leak. If the system is well-outgassed and leak-free, you are ready to begin the experiment.

Pumping Out the Manifold when the Diffusion Pump is Hot

1. If the pressure is less than 200 microns, the gas can be pumped out through the hot diffusion pump by opening valve B with valve A also open and valve C shut. If the manifold has gas at a pressure of 200 microns or higher that needs to be pumped out, it should be done so directly with the mechanical pump with the diffusion pump isolated. Do so by the following steps:
 2. Shut valves A and B, if not already shut.
 3. Open valve C and wait for the pressure to fall to below 200 microns.
 4. Shut valve C.
 5. Open valves A and B.

Admitting Pure Gas Samples

1. The small gas cylinders filled with 1 atm or less of a gas should provide more than enough gas for several runs. If you need to fill these cylinders use the baratron gauge to admit less than 1 atm (760 torr) to the entire gas manifold including the cylinder you wish to fill. Obviously, valves B, C, and D must be closed to do so. If the cylinders are already filled, go directly to step 3.
2. Close the valve on the cylinder, then pump out the gas from the manifold according to the above procedure.
3. Make sure the manifold is completely pumped out and that the pressure is constant at a low value when it is not being pumped, i.e. with valves B, C, and D shut.
4. Admit gas to the manifold in two stages by first shutting the manifold valve directly above the cylinder containing the gas you will use. Then briefly open then shut the cylinder valve to admit gas only to the region between the cylinder valve and the manifold valve (either E or F).
5. While carefully watching the reading from TC1, slowly open the manifold valve just enough to bring the pressure in the manifold to 200-500 microns. Then shut the manifold valve.
6. Once the pressure has stabilized to a constant value, open valve D. The gas should then begin effusing through the pinhole above valve D. Record the pressure as a function of time. Exactly how often you should record the pressure depends on how quickly the

pressure changes. For a heavy gas, a small pinhole, every 5 minutes might be sufficient near the end of a run. For a light gas, a larger pinhole, and a high initial pressure, every two or three seconds might be appropriate. Record the pressure until it has fallen to at least 25% of its initial value or until it no longer changes with time.

7. Exactly the same procedure can be used to determine the relaxation constant for an unknown gas.