

# LOW PRESSURE EFFUSION OF GASES

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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.

## I. 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 of molecules with the 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.

## II. 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 Maxwell-Boltzmann speed distribution function:

$$\frac{dN}{N} = 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} c^2 e^{-mc^2 / 2kT} dc \quad (1)$$

where  $\frac{dN}{N}$  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:

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

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 (their speed and direction): 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 speed distribution function. Integrating over all velocities and pertinent directions a collision frequency per unit area can be expressed in terms of the average speed,

$$\Gamma_{\rho} = \frac{1}{4} \rho \langle c \rangle \quad (3)$$

$$\Gamma_{\rho} = \rho \left( \frac{kT}{2\pi m} \right)^{1/2} \quad (4)$$

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

$$\Gamma_{n/V} = \frac{n}{V} \left( \frac{RT}{2\pi M} \right)^{1/2} \quad (5)$$

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

$$\Gamma_P = \frac{P}{\sqrt{2\pi MRT}} \quad (6)$$

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,  $\Gamma_P$  times the area of the orifice,  $A$ . In terms of moles of gas lost per unit time:

$$\frac{dn}{dt} = \frac{-AP}{\sqrt{2\pi MRT}} \quad (7)$$

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. (7) rearranges to

$$\frac{dP}{P} = -\frac{A}{V} \left( \frac{RT}{2\pi M} \right)^{1/2} dt \quad (8)$$

$$= -C dt \quad (9)$$

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

$$P = P_0 e^{-Ct} \quad (10)$$

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 N<sub>2</sub>. 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.

### III. 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 0 K. Choose N<sub>2</sub> as the molecule. What is the most probable speed for a nitrogen molecule at 300 K? 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 0 K to 100 K. How does this curve compare to the 300 K 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 1000 K. Print this plot of the three speed distributions at 100, 300, and 1000 K. Return all temperature dials to 0 K except the 300 K one. Change the molecule to H<sub>2</sub> and I<sub>2</sub>. 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.

## IV. Lab Report

Your lab report should include the following:

1. Prepare four plots, two showing data for He runs and two for N<sub>2</sub> 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 table 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 following lab period 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,  $M_{\text{unk}} = 28 [C_{\text{N}_2}/C_{\text{unk}}]^2 = 4 [C_{\text{He}}/C_{\text{unk}}]^2$ , where *C*<sub>N<sub>2</sub></sub> and *C*<sub>He</sub>, are the relaxation constants for N<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub>. 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<sub>2</sub>? From the mass and uncertainty that you determined for the unknown gas, indicate how certain you are of the identity of the unknown gas.

## V. 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 value. 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. Why did we develop our model in terms of a distribution of molecular speeds rather than a distribution of molecular velocities? What is the average velocity for your sample of N<sub>2</sub>?

## VI. 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 Ball valve, which opens and shuts with only a 90° turn; turn clockwise to shut, counterclockwise to open. The handle indicates whether the valve is in the opened or closed position. Handle “in line” is open; handle at 90° is closed. There are four Ball valves on the system (valves A, B, C, and the service valve). **The top Ball valve is a “Service Value” and should always be open.** 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 it should be handled with care. The bellows

valves generally should not be opened all the way but should be left with about a  $10^\circ$  turn from fully open. Note that valve D is the only valve that needs to be fully open in the beginning of the experiment. There is one baratron vacuum gauge and three thermocouple (TC) 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  $7.6 \times 10^5$  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 about 24 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.

### **Pumping Out Manifold when Mechanical Pump is Running**

During the semester, the apparatus should be left under vacuum. However, if the entire system needs to be pumped down from atmosphere, have your TA perform that procedure for you before you begin the experiment.

If manifold pressure is below 30-50 microns, the diffusion pump can be started using the following procedure. (If pressure is higher follow directions in **Pumping Out Manifold when Diffusion Pump is Hot** section below.)

1. Make sure water is flowing through the DP cooling coils.
2. Close valve C. Open valve B. (Valve A should be open. If valve A is closed, open it before opening valve B.)
3. Turn on diffusion pump. The oil in the DP gives off gases as it heats up, known as out-gassing, so the manifold pressure may initially rise and then, after a few minutes, fall.
4. Wait 10-15 minutes for the DP to reach optimal operating temperature.

5. Ideally the pressure should be below 10 microns before starting experiment but practically one can start with pressures as high as 25-30 microns. If pressure is higher follow directions in **Pumping Out Manifold when Diffusion Pump is Hot** section below.

### Admitting Pure Gas Samples

1. Make sure manifold is completely pumped out and pressure constant at a low value when it is not being pumped, *i.e.*, with valves B, C, and D shut. Note that here valve A is open.
2. Admit gas to the manifold in two stages:
  - a. Values E, F and G should be closed.
  - b. Briefly open then shut the valve to the cylinder (containing the gas which you will use) to admit gas to the region between the cylinder valve and the manifold valve (value E, F, or G).
  - c. Quickly open then close valve E, F, or G to fill manifold to 500-600 microns.
  - d. If pressure reading on thermocouple gauge is 1, pump manifold with mechanical pump until proper pressure is achieved. **At this point be extra careful to close valve A before opening valve C, to prevent back effusion into manifold.**
  - e. The cylinder valve and manifold valve should never be open at the same time.
3. Once pressure has stabilized to a constant value, open valve D. The gas should then begin effusing through the pinhole above valve D. Record pressure as a function of time. Exactly how frequently you should record depends on how quickly the pressure changes. For a heavy gas, a small pinhole, every 5-10 seconds 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 falls to at least 25% of its initial value or until it no longer changes with time (*e.g.*,  $P_0 = 500$  microns,  $P_f = 125$  microns).
4. Close valve D when the pressure falls to 25% of its initial value or until it no longer changes with time.
5. The same procedure, beginning with step 1, is used for the unknown gas.
6. At the end of each trial the pressure will exceed 100 microns in the manifold. In order to pump down, isolate the DP by closing valve A then open valve C to pump with only the MP.



7. When pressure has fallen below 100 microns and stabilized, close valve C to prevent back effusion. The gas can then be pumped out through the hot DP by first opening valve A and then valve B.

### **Pumping Out Manifold when Diffusion Pump is Hot**

If the pressure is less than 100 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 100 microns or higher that needs to be pumped out, it should be done so directly with the mechanical pump with the diffusion pump isolated for a short time. Do so by the following steps:

1. Shut valves A and B, if not already shut.
2. Open valve C and wait for the pressure to fall to below 100 microns (closer to 25 microns).
3. Shut valve C.
4. Open valves A and B.

### **Shutting Down Experiment**

1. Make sure that valves E, F, G, and D are closed.
2. The mechanical pump **should be left on**.
3. Water should be flowing through the diffusion pump cooling coils.
4. Follow Shut Down Procedure on Manifold.

### **WARNINGS!!**

1. **Never open valves B and C at the same time**
2. **Never close valve A while valve B is open**
3. **Never open valve A while valve C is open (this is only done at the end of the experiment when there is no gas in the manifold)**

# Gas Effusion Apparatus

