

Vapor Pressure of a Solid by Knudsen Effusion

Readings: Atkins (8th ed) pages 127-128 and 746-757; Garland, Nibler, and Shoemaker (GNS) (8th ed) pages 119-127, 587-594, and 597.

Introduction

Methods of measuring vapor pressure can be divided into direct methods and indirect methods. In a direct method, the actual pressure in the pure equilibrium vapor is determined, and the main experimental questions have to do with choice of manometer, sample purity, and how to be sure of equilibrium conditions. For indirect methods, some property related to the vapor pressure is measured, and the experimental questions have to do with whether the experiment satisfies the conditions under which the property actually has a theoretical relationship(s) to the vapor pressure. The Knudsen effusion method is such an indirect method and is well-suited for low vapor pressures.

In the Knudsen effusion method, a sample is held in a capsule with a small hole in its wall. The sample is assumed to maintain its equilibrium vapor pressure inside the capsule. The capsule is held in a vacuum space. Vapor molecules leak out of the capsule into the vacuum. It is assumed that the rate of molecules escaping through the hole equals the rate at which molecules would strike an area of wall equal to the hole area if the hole were closed. This assumption will be correct if the mean free path (λ) of vapor molecules is long compared to the radius of the hole. (The mean free path is the average distance gas molecules travel between collisions. The vacuum is necessary to keep air molecules from limiting the mean free path of the vapor molecules. A low vapor pressure then ensures a long mean free path.) The number of molecules escaping can be found from the mass loss of the sample and its molecular mass.

The frequency of collisions of gas molecules with the a wall per unit wall area is given by

$$Z_{wall} = \frac{n\bar{c}}{4}$$

where n is the number density and \bar{c} is the average speed. (The number density is the ratio of the total number of gas molecules to the total gas volume.)

The ideal gas law (using the number density and the number of particles) is, $P = nkT$, where k is Boltzmann's constant. Also,

$$\bar{c} = \sqrt{\frac{8kT}{\pi m}}$$

where m is the molecular mass. (See Appendix I for derivation.)

If a hole of area A is cut in the wall, and if the hole does not disturb the velocity and density distribution in the gas, the number of molecules entering the hole in time t will be

$$number = Z_{wall} At .$$

If the molecules entering the hole are permanently lost from the gas to a vacuum space on the other side of the hole, then the total mass lost from the gas will be

$$\text{mass lost (g)} = m(\text{number}) = mZ_{\text{wall}}At$$

and

$$P = \frac{g}{At} \sqrt{\frac{2\pi kT}{m}} = \frac{g}{At} \sqrt{\frac{2\pi RT}{M}}$$

where R is the universal gas constant and M is the molar mass.

The velocity and density distributions will not be disturbed by the leak through a hole if the mean free path is large compared with the hole radius. (See Appendix II for an approximate derivation.) The mean free path is given by

$$\lambda = \frac{kT}{\sqrt{2}P\sigma}$$

where σ is the collision cross-section, given by $\sigma = \pi d^2$ and d is the effective molecular diameter.

Holes with non-zero length complicate the theory. A molecule may enter the hole, strike the hole wall, and go back into the vapor space instead of going out. The effective area of the hole then becomes Af where f is a correction factor called the Clausing factor and depends on the ratio of hole length to hole radius. Iczkowski *et al.* give the following Clausing factors for cylindrical holes:

l/r	f
0.0	1.00
0.1	0.952399
0.2	0.909215
0.5	0.801271

and can be approximated by $f = 1 - 0.5(l/r) + 0.2(l/r)^2$ while the thickness of the lids of our cells is 0.013 cm. Taking the lid thickness as the hole length (l) you can find the Clausing factors needed.

Experiment

Use the Knudsen effusion method to measure the vapor pressure of p-bromonitrobenzene at 35° and at 50°. Calculate the enthalpy of sublimation.

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H}{R} \left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

Calculate heats of vaporization from Swan and Mack's vapor pressure data for the temperature intervals 25°- 35° and 40° - 50°. Compare your results for vapor pressure and enthalpy of sublimation with the results from Swan and Mack. (Suggestion: Compare your enthalpy of sublimation with the results calculated from Swan and Mack's equation for 35° - 50°. Estimate the heat capacity difference between solid and vapor indicated by the change in the Swan and Mack enthalpy of sublimation with temperature. Estimate the maximum heat capacity one might expect for this substance as vapor and as solid, using classical equipartition theory. See GNS pp. 106-109. The equipartition value is $R/2$ for each degree of freedom plus $R/2$ extra for each vibration. In the solid there are 3N vibrations, while in the gas there are 3N-6 vibrations for nonlinear molecules. Compare this heat capacity difference with the value indicated by change in enthalpy of vaporization in a 15° temperature change from Swan and Mack's data. At the end you should be able to reach some conclusions about the relative quality of your data versus the Swan and Mack data.)

Sample Handling

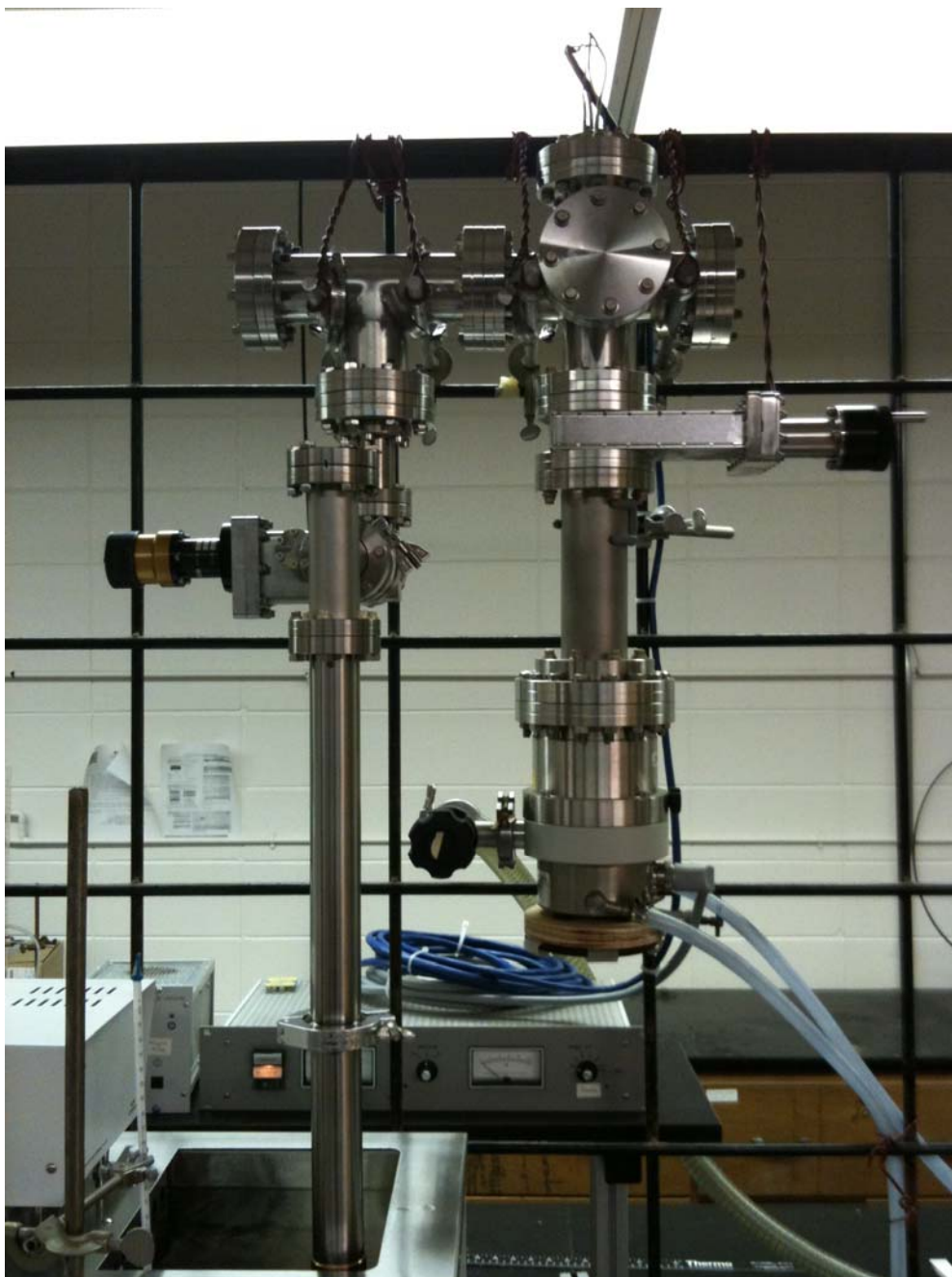
The solid used in this experiment, p-bromonitrobenzene, is kept in a bottle stored in a small desiccator. Enough sample should be put into the sample cell to cover the bottom of the cell. The cell cover should be screwed on, and the whole assembly should be weighed (to the nearest 0.0001g.) The cell and contents should be weighed after the experiment to find the mass of sample that escaped from the cell. (The cell should be at room temperature for both weighings.) At the end of the experiment, the excess sample should be put in the bottle marked "Recycle p-bromonitrobenzene".

Vacuum System

The vacuum system used for this experiment uses a mechanical vacuum pump and a turbomolecular (turbo, for short) pump. The mechanical pump is in the cabinet under the bench. The pressure during the experiment is read with an ion gauge. A picture of the main vacuum chamber is at the top of the following page. The mechanical vacuum pump is called the forepump and is used in conjunction with the turbo. Bulk air is pumped out through the turbo pump with the forepump while it is spinning up to its operating speed.

General Operating Instructions for the Vacuum System

1. Consult an instructor in case of any problems.
2. The turbo pump should be pumping on the system and the pressure should be less than 10^{-5} Torr.
3. The only valve that you will need to turn is the black/gold one shown in the following two pictures.



Starting a Run (*The 50 °C should be done on Tuesday and the 35 °C run should be completed on Thursday.*)

1. Turn on the bath heater and stirrer and adjust the controller to the desired temperature.
2. Clean and dry the cell and cell holder. A thorough wipe with a Kimwipe usually will do. Don't use water. If a solvent is needed, use hexane.

- Put enough sample in the cell to cover the bottom with a thin layer. (0.2 grams should be enough.) Put the cap on the cell. Use the cap with the smaller hole for the 50° C run; use the cap with the larger hole for the 35° C run. Wipe the cell carefully and weigh it. (Keep finger prints off the cell as they have a measureable mass. You might want to wear gloves.)



- Put the cell in the bottom of the cell holder. (The cell holder is the large copper tube with the stainless steel top.)
- Connect the cell holder to the cold finger with the KF flange and tighten the clamp.
- Turn off the ion gauge and open the black\gold-handled valve. There will be a red nub showing when the valve is completely open. The pressure should fall rapidly.
- Start timing when you open the valve.

8. Add an inch or two of liquid N₂ to the cold finger. (Completely fill the cold finger about five minutes later.) Turn the ion gauge back on after the turbo speed indicator is fully lit.
9. The total run time should be at least 2.5 hours for the 50°C run and at least 3 hours for the 35°C run. Keep liquid nitrogen level up. Check the water bath temperature regularly. (Read thermometer to 0.01°C. Write each reading in your notebook.)

Ending a Run

1. Close the black\gold-handled valve and stop timing.
2. Loosen the KF flange clamp.
3. Remove cell holder.
4. Remove cell. Wipe it off. Let it cool.
5. Turn off the bath stirrer and heater.
6. Remove the cold finger by loosening the other KF flange clamp and pour out the remaining liquid nitrogen. Set the cold finger aside and allow it to warm to room temperature below cleaning.
7. Weigh the cell with then lid on after it comes to room temperature.
8. Dump sample into recycle bottle.
9. Measure diameter of hole in cell lid, if you have not already done so.
10. Set the ion gauge controller to the 10⁻⁴ Torr setting.

Measuring the Diameter of the Hole

The binocular microscope located in the X-ray lab has a graduated scale in the eye lens. *Check the scale by looking at a scale on a good ruler.* (There should be an accurate scale for comparison in a small black case in the drawer under the vacuum system.) Measure the hole diameter by looking at the hole from both the front side and the back side. Measure the diameter in at least three different directions on each side.

Appendix I

Frequency of Wall Collisions and Average Speed of Gas Molecules

A Simplified Model

Assume that the gas molecules are uniformly distributed in space (number density n) and that all molecules move at the same speed, c . Assume $1/6$ of the molecules move parallel to each of the positive and negative directions of a Cartesian (x - y - z) coordinate system. A wall in the y - z plane is struck on one side by molecules coming from the $x > 0$ direction and moving towards negative x . The molecules starting with $0 < x < ct$ are close enough to strike the wall in a time interval t . The total number of collisions in time t on an area A of the wall is

$$(1/6) nAct = Z_{\text{wall}}At$$

so

$$Z_{\text{wall}} = nc/6.$$

An Accurate Kinetic Theory Model

The effect of molecular collisions on the equilibrium properties of gases can be ignored so long as the total effective volume of the molecules is small compared with the total volume of the gas. The pressure a gas exerts on a solid wall is such an equilibrium property. It depends on the frequency of molecular collisions with the wall and on the average momentum carried by the molecules striking the wall. The velocity distribution is the same everywhere in an equilibrium gas. Any small volume of gas, $d\tau$, will have molecules coming in and molecules going out. Some of the molecules coming in will go right on through without making a collision with another molecule, and those then become molecules going out of the volume $d\tau$. Other molecules entering the volume $d\tau$ will make a collision, which will generally change both the speed and direction of each such molecule. However, on average, some molecule going out of $d\tau$ after making a collision will have the same speed and direction as one of the molecules that came into $d\tau$ and made a collision. So, we can go ahead and calculate molecular collision frequency with the wall without considering molecule - molecule collisions in the gas phase; as long as we are dealing with an equilibrium gas.

The velocity distribution, $f(c)$, when multiplied by $dc_x dc_y dc_z$, gives the fraction of molecules having velocity components in the interval c_x to $c_x + dc_x$, c_y to $c_y + dc_y$, and c_z to $c_z + dc_z$. It is

$$f(c_x, c_y, c_z) = \left(\frac{m}{2\pi kT} \right)^{3/2} \exp\left(-\frac{m(c_x^2 + c_y^2 + c_z^2)}{2kT} \right)$$

(The exponential is the Boltzmann factor for the kinetic energy. The factors in front make $f(c)$ integrate to 1 when the distribution is integrated over the full infinite ranges in c_x , c_y , and c_z .)

The average speed is found by multiplying $f(c)$ by $|c|$ and integrating over the full infinite range in c_x , c_y , and c_z . The integration can be carried out in spherical polar coordinates:

$$\bar{c} = \int_{c=0}^{\infty} c \cdot f(c) \cdot dc = \left(\frac{m}{2\pi kT} \right)^{3/2} \int_0^{\pi} \sin(\theta) d\theta \int_0^{2\pi} d\phi \int_{c=0}^{\infty} c^2 dc \cdot c \cdot \exp\left(-\frac{mc^2}{2kT}\right)$$

$$\bar{c} = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} \int_{c=0}^{\infty} c^3 \exp\left(-\frac{mc^2}{2kT}\right) dc$$

The result of integration is the average speed,

$$\bar{c} = \sqrt{\frac{8kT}{\pi m}}.$$

The wall collision frequency can be found as follows: Take a small area dA on a plane solid surface. Make the center of dA the origin of a spherical polar coordinate system with the z -axis outward and perpendicular to dA . Consider a volume element $d\tau = r^2 \sin(\theta) dr d\theta d\phi$ located at (r, θ, ϕ) . Some of the molecules in this volume element at time zero will travel far enough to strike dA in a time interval t ; these molecules have speeds greater than r/t . They also must be traveling toward dA . The fraction of molecules in $d\tau$ that are traveling toward dA is $dA \cos(\theta) / 4\pi r^2$. So the molecules originally in $d\tau$ that strike dA in the time interval t are the ones going in the right direction and are fast enough to get there. The number of molecules striking dA in time t is

$$(\text{number}) = \frac{n \cdot dA \cdot \cos(\theta)}{4\pi r^2} \left(\frac{m}{2\pi kT} \right)^{1/2} \int_{r/t}^{\infty} 4\pi \cdot c^2 dc \cdot \exp\left(-\frac{mc^2}{2kT}\right)$$

Now, if we integrate this number over all volume elements above the surface, so that $0 \leq \theta \leq \pi/2$, we get $dA \cdot t \cdot Z_{\text{wall}}$. We get a factor of π upon integrating over the angles. We are left with a double integral over the full semi-infinite range in r and the range above in c . The whole business can be handled by reversing the order of integration, doing the integral on r from zero to $c \cdot t$ and then doing the integral on c over the full semi-infinite range. The result rearranges to

$$\bar{c} = \sqrt{\frac{8kT}{\pi m}}$$

Appendix II

Mean Free Path and Hole Size

Assume that the molecules escaping through the hole make their last collisions before entering the hole at a distance of one mean free path from the hole. Call the region where escaping molecules make their last collisions the “source region.” Also, assume that molecules always travel one mean free path between collisions. (Walls are assumed to reflect molecules, so

walls don't affect the picture.) The hole disturbs both the density and the velocity distribution in the source region because molecules don't come back to the source region from the hole, lowering the density, and molecules don't come from the direction of the hole, which disturbs the velocity distribution. The missing number density will be approximately $nA''/(4\pi\lambda^2)$ where A'' is the effective area of the hole (A') projected onto a sphere of radius λ centered at each point in source region. The average error in the pressure in the source region will be given by $(\Delta P/P)=(A'/6\pi\lambda^2)$ when we average over all source directions. If we take A' as $f\cdot A = f\pi R^2$, where f is a Clausing factor and R is the radius of the hole, then

$$\frac{\Delta P}{P} = \left(\frac{f}{6}\right)\left(\frac{R}{\lambda}\right)^2.$$

With $f=0.9$ and $\lambda>2R$ we have $(\Delta P/P) < 0.0375$. This is something of an over-estimate of the error, since more wall collisions are made by faster-moving molecules than by slower ones, and faster-moving molecules have longer mean free paths than slower ones. Also, molecules tend to continue moving in the same general direction after collision as before. (This is called "the persistence of velocities.") So, a molecule that goes out the hole most likely came from somewhere away from the hole at an effective distance larger than one mean free path.

The expression above should be used to form an opinion as to the suitability of the experiment for the measured vapor pressure. It is not useful for correction of results because it is only a rough approximation; also, molecular diameters suitable for calculating mean free paths are only approximately the same size as molecular diameters from other sources, such as density of solids. (As a cautionary example, one might consider Example 24.3 in Atkins (7th ed) on p. 826. At the pressure given the mean free path of Cs atoms must be of the order of 0.01-0.001 mm, far smaller than the hole diameter of 0.5 mm. So the conditions for Knudsen effusion are not met at all!)

References

General: See Kinetic Theory of Gases, Mean Free Path, Maxwell Velocity Distribution, Collision Frequency in the index of any good standard physical chemistry textbook.

Method: G.W. Thomson, pp. 460-463, "Physical Methods of Organic Chemistry," Part I, A. Weisberger, ed. New York, 1959.

Example: Swan, T.H. and E. Mack, Jr., *J. Am. Chem. Soc.* **1925**, 47, 2112.

Clausing Factor: Ickowski, R.P., J.L. Margrave, and S.M. Robinson, *J. Phys. Chem.* **1963**, 67, 229.

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