

## VAPOR PRESSURE OF A SOLID BY KNUDSEN EFFUSION 2002

### 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. In an indirect method, some property related to the vapor pressure is measured, and the experimental questions have to do with having the experiment satisfy the conditions under which the property actually has the theoretical relation to the vapor pressure. The Knudsen effusion method is such an indirect method, 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 (  $\lambda$  ) of vapor molecules is long compared with 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 the molecular mass.

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

$$Z_{\text{wall}} = n\bar{c} / 4$$

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

The ideal gas law is  $P = nkT$  where  $k$  = Boltzmann's constant.

Also,

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

where  $m$  = 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

$$\text{number} = Z_{\text{wall}}At$$

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

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

and

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

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 the 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

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

where  $\sigma$  is the collision cross-section, given by  $\sigma = d^2$  with  $d$  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  $A f$  where  $f$  is a correction factor called the Clausing factor and depends on the ratio of hole length to hole radius. (See the posted chart.)

### Experiment.

Use the Knudsen effusion method to measure the vapor pressure of p-bromonitrobenzene at 30° and at 40°. Calculate the enthalpy of sublimation.

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

Calculate vapor pressures at 30° and at 40° using Swan and Mack's vapor pressure equation. Calculate heats of vaporization from Swan and Mack's vapor pressure equation for the temperature intervals 20° - 30° and 30° - 40°. 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 30° - 40°. 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 SGN pp. 104-107. 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 10° 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.)

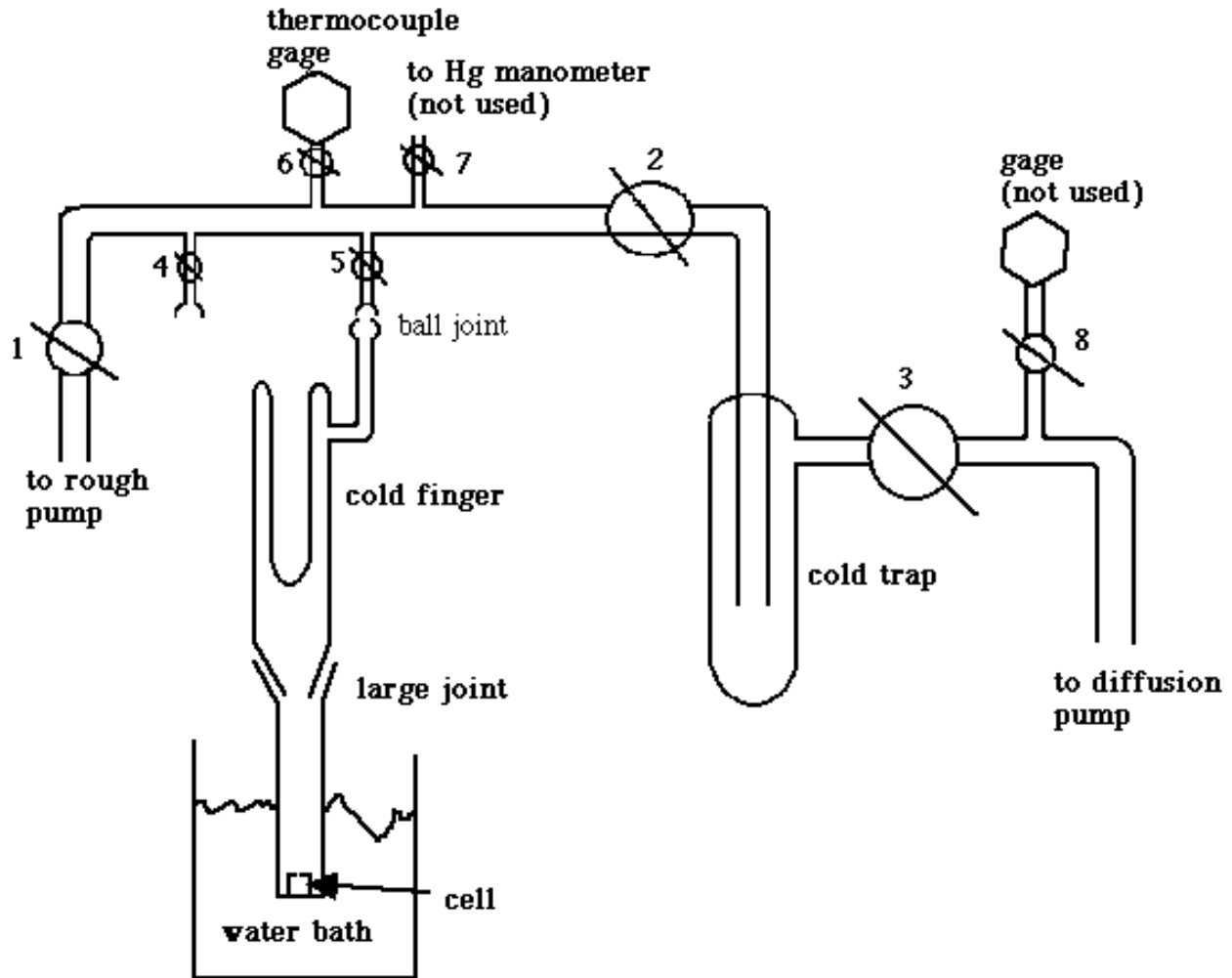
### Sample Handling.

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. The cell and contents should be weighed after the experiment to find the mass of sample that escaped from the cell. 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 two mechanical vacuum pumps, an oil diffusion pump, and a liquid nitrogen cold trap. The mechanical pumps are in the cabinet under the bench. The pressure is read with a thermocouple gage. (See SGN pp. 688-694, 701.) One of the vacuum pumps is connected to the left end of the system. This is the rough pump. Bulk air is pumped out through the rough pump until a fairly low pressure is reached. The system is then disconnected from the rough pump and connected through the liquid nitrogen trap to the diffusion pump at the right end of the system. The diffusion pump only operates when the total system pressure is below the boiling pressure of the diffusion pump oil, so the second mechanical pump (the fore pump) backs the diffusion pump by removing gas from the outlet of the diffusion pump. The liquid nitrogen trap keeps oil vapor out of the rest of the system and also condenses water vapor and carbon dioxide.

Air will oxidize hot diffusion pump oil, and pumping lots of air through a mechanical pump tends to degrade the pump oil and the pump itself. Pump air to the left (to the rough pump.) Pump to the right to get a high vacuum after most of the air is gone.



#### General

1. Stopcocks #1, #2, #3 are open when the hole in the plug lines up with the side tube. Stopcocks #4-8 are open when the tube through the plug lines up with the side tubes.
2. Stopcocks #4-8 have hollow plugs that are evacuated through a small hole. Do not turn the plug 180° away from the open position unless the plug is to be evacuated.
3. Turn stopcocks slowly with moderate torque. The side tubes carry the force you apply. Quick turns may break the tubes or pop the plug out of the body.
4. Stopcocks #7 and #8 should be closed at all times.

## Vacuum System Start-Up

1. Make sure #3, #4, and #5 are closed.
2. Turn on the rough pump and the fore pump.
3. Look at the pumps to be sure they are running. Leave one of the cabinet doors open while the mechanical pumps are running.
4. Open #1 and #2. Open #6 and turn on the gage. Turn on the diffusion pump and turn on the diffusion pump cooling water. The pump boiler will get hot in 15 minutes. (If pressure does not fall to less than 100 microns, turn off the diffusion pump before the boiler gets hot.) (The fan should be off until the end of the experiment.)
5. When pressure falls below 200 microns, open #3 and close #1. Pressure should continue to fall. (Consult an instructor in case of any problems.)
6. Mount a Dewar flask around trap, pour in a little liquid N<sub>2</sub>, let cool for about 2 minutes, raise N<sub>2</sub> depth to about 2 inches. Pressure should soon fall below 10 microns.

### Summary:

The system is pumped to a low pressure with the rough pump. This keeps air out of the fore pump. The diffusion pump is hot only when the pressure is low. This keeps air from burning the hot diffusion pump oil. Don't pump air through a hot diffusion pump.

### Starting A Run

1. Turn on the bath heater and stirrer and set the contact thermometer to slightly below the desired temperature. Turn on the vacuum system. (See above.)
2. Clean and dry the cell and cell holder. A thorough wipe with a Kimwipe usually will do. Don't use water. If solvent is needed, use hexane.
3. 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 40° C run, use the cap with the larger hole for the 30° C run. Wipe the cell carefully and weigh it. (Keep finger prints and vacuum grease off the cell.)
4. Put the cell in the bottom of the cell holder. (The cell holder is a large copper tube with a glass tube cemented on top. It has a ground joint at the end. The stuff inside that looks like grease on the glass is actually set epoxy cement.)
5. Grease the large ground joint with six thin vertical stripes of Apiezon M grease.
6. Join the cell holder to the cold finger. Twist back and forth through very small arcs to spread the grease film. (Just wiggle the two a little.)
7. Apply 4 thin strips of grease to the ball joint. Mount cell holder in the bath with a large clamp. (The ball joint should be joined.)
8. After the cell holder is firmly clamped in place, clamp the ball joint.

9. Close stopcock #2, open #1. Open #5. Pressure should fall rapidly. When pressure falls below 200 microns, close #1 and open #2. Your run is now starting.
10. Start timing when pressure falls below 20 microns. (Pressure should fall to near zero in 5 minutes or less.)
11. Add about one inch liquid N<sup>o</sup> to the cold finger. (Increase depth to 2-3 inches about five minutes later.)
12. Run time should be about 2 hours. Keep liquid nitrogen levels up. Check bath temperature regularly. (Read thermometer to 0.01°C.)

### **Ending A Run**

1. Close stopcock #2. Open #4 and stop timing.
2. Unclamp ball joint.
3. Remove cell holder and cold finger.
4. Detach cold finger and pour liquid N<sub>2</sub> into supply Dewar.
5. Remove cell. Wipe it off. Let it cool.
6. Turn off the bath stirrer and heater.
7. Weigh the cell with then lid on after it comes to room temperature.
8. Dump sample into recycle bottle.
9. Shut down vacuum system.
10. Measure diameter of hole in cell lid, if you have not already done so.

### **Vacuum System Shut-Down**

1. Turn off diffusion pump heater.
2. Turn on fan to cool diffusion pump.
3. Close stopcocks #4, #5. Open #1.
4. Remove trap Dewar. Dump liquid N<sub>2</sub> into supply Dewar. (Leave the trap Dewar upside down on the bench top. Leave the Dewar support under the trap, just in case the bottom of the trap decides to fall off.)
5. Close #3, open #2.
6. When diffusion pump is cool enough to hold a finger on, and trap melts off the ice, close #1.
7. Turn off fan, mechanical pumps, and diffusion pump water.

8. Put everything away clean and free of grease.

### Measuring Diameter of 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. Measure hole diameter by looking at the hole from both the front side and the back side. Measure 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 the gas molecules are uniformly distributed in space (number density  $n$ ) and all move at the same speed,  $c$ . Assume  $1/6$  of the molecules move parallel to each of the positive and negative coordinate directions of a cartesian ( $x$ - $y$ - $z$ ) axis system. A wall in the  $y$ - $z$  plane is struck on one side by molecules coming from  $x > 0$  and moving toward 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,  $d$ , 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  $d$ . Other molecules entering the volume  $d$  will make a collision, which will generally change both the speed and direction of each such molecule. However, on the average, some molecule going out of  $d$  after making a collision will have the same speed and direction as one of the molecules that came into  $d$  and made a collision. So, we can go ahead to calculate molecular collision frequency with the wall without considering molecule-molecule collisions in the gas phase, so long as we are dealing with an equilibrium gas.

The velocity distribution,  $P$ , 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

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

(The exponential is the Boltzmann factor for the kinetic energy. The factors in front make  $P$  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  $P$  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:

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

to give

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

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 perpendicular to  $dA$ . Consider a volume element  $dV = r^2 \sin(\theta) dr d\theta d\phi$  located at  $(r, \theta, \phi)$ . 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 travelling toward  $dA$ : the fraction of molecules in  $dV$  that are travelling toward  $dA$  is  $dA \cos(\theta) / 4\pi r^2$ . So the molecules originally in  $dV$  that strike  $dA$  in the time interval  $t$  are the ones going in the right direction and fast enough to get there: the number striking  $dA$  in time  $t$  is

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

Now, if we integrate this number over all volume elements above the surface, so that  $\theta$  goes from  $0$  to  $\pi/2$ , we get  $dAtZ_{wall}$ . We get a factor of  $\pi$  on 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  $ct$  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 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 molecules always travel one mean free path between collisions. (Walls are assumed to reflect molecules, so the 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  $nA''/(4\pi R^2)$  where  $A''$  is the effective area of the hole ( $A'$ ) projected onto a sphere of radius  $R$  centered at each point in source region. The average error in the pressure in the source region will be given by  $(\Delta P/P) = (A'/6\pi R^2)$  when we average over all source directions. If we take  $A'$  as  $f \cdot A = f \cdot \pi R^2$ , 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 an approximate expression, and 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.

#### 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.

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