

Vapor Pressure and Molecular Weight of a Pure Liquid

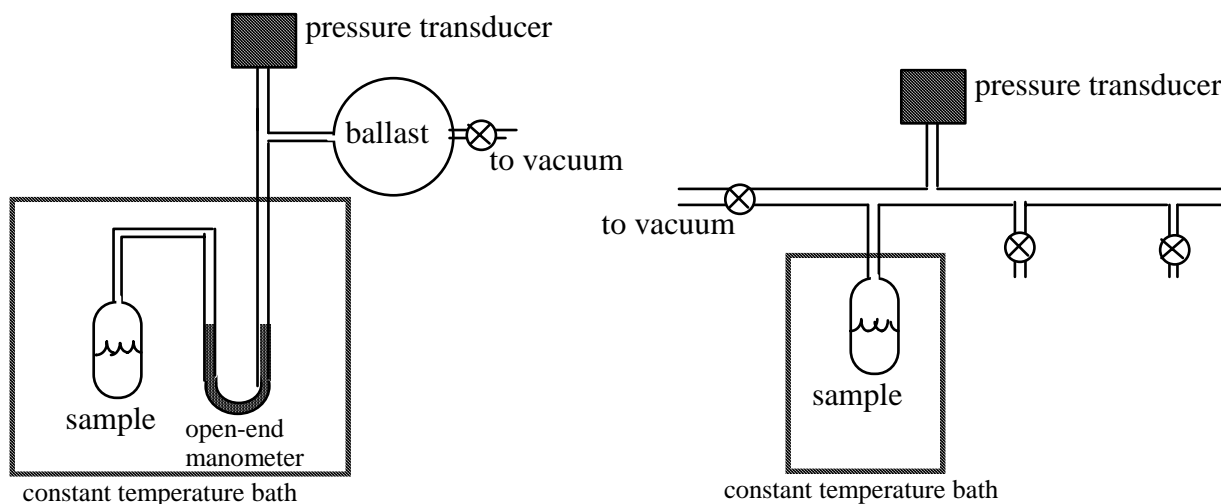
Purpose

The purpose of this lab is to measure the enthalpy and entropy of vaporization of n-pentane. You will also determine the molecular weight of pentane. A secondary purpose is to familiarize you with the operation of a vacuum line.

Introduction

Vapor pressure and enthalpy of vaporization are important properties of a volatile substance. Vapor pressures are needed to understand distillation and other separation techniques. The enthalpy of vaporization is necessary to predict the change in boiling point with pressure. The enthalpy and entropy of vaporization are needed to calculate the enthalpy, absolute entropy, and Gibb's free energy of formation of gaseous substances. These thermodynamic variables are also important measures of intermolecular interactions.

Vapor pressures are most accurately measured with an isoteniscope, Figure 1a. A small bulb holding the substance is attached to a open-end manometer. The sample bulb and the open-end manometer are both held in a constant temperature bath. The vapor pressure of the liquid is measured by adjusting the pressure in the ballast bulb so that the level of the manometer is the same in both arms. Then the pressure in the sample bulb is the same as in the ballast bulb, and the pressure of the ballast bulb is then recorded. The advantage of the isoteniscope is that the liquid and vapor of the sample are both kept at the constant temperature.



a. Isoteniscope

b. Vacuum line

Figure 1. Vapor pressure measurement: (a) isoteniscope, (b) vacuum line. In a vacuum line part of the vapor is at room temperature, causing a temperature gradient.

A less accurate, but more common method for measuring vapor pressures is a vacuum line, Figure 1b. Vacuum lines are used in handling gases and air or moisture sensitive compounds. Inorganic chemists often use vacuum lines for synthesis and characterization. For simple compounds, vapor pressure and enthalpy of vaporization are often used for quick characterization of unknowns. Therefore, a vacuum line is an important piece of laboratory apparatus that every chemist should know how to use.

In a vacuum line, the vapor pressure of the substance is directly measured by the pressure transducer. In other words, the substance comes in direct contact with the pressure measurement device, since there is no intervening open-end manometer. Therefore, most of the vapor is at a different temperature than the liquid. This temperature gradient makes true equilibrium impossible to establish, and also the properties of the gas are different in different parts of the vacuum line. These effects cause systematic errors in the vapor pressure measurement. However, the speed and convenience of using the vacuum line method usually outweigh these errors.

The procedure for the vacuum line is very simple. The sample is placed in a constant temperature bath; after the pressure stabilizes, the pressure is recorded. To give you some practice in using the vacuum line, you will also experimentally determine the molecular weight of the substance using a vapor density measurement.

Theory

The relationship between vapor pressure and temperature is given by the Clausius-Clapeyron equation:

$$\ln \left(\frac{p_2}{p_1} \right) = \frac{-\Delta_{\text{vap}}H_m}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (1)$$

The assumptions used in the derivation of eq. 1 are that the vapor behaves as an ideal gas, the molar volume of the liquid is much smaller than the vapor, and the enthalpy of vaporization is independent of temperature. For this experiment we need to relax the assumption that the vapor behaves ideally. We also need to consider the effects of the assumption that the enthalpy of vaporization is independent of temperature.

Please review the derivation of the Clapeyron equation in your text. The Clapeyron equation applies to the equilibrium vapor pressure curve:

$$\frac{dp}{dT} = \frac{\Delta_{\text{vap}}S_m}{\Delta_{\text{vap}}V_m} \quad (2)$$

where $\Delta_{\text{vap}}S_m$ and $\Delta_{\text{vap}}V_m$ are the change in molar entropy and molar volume for the phase transition (vapor -liquid). At equilibrium the vaporization process is reversible and isothermal so that the entropy of vaporization is:

$$\Delta_{\text{vap}}S_m = \Delta_{\text{vap}}H_m / T \quad (3)$$

Substituting eq. 3 into eq. 2 and assuming that the volume of the liquid is negligible compared to the vapor so that $\Delta_{\text{vap}}V_m = V_m$, the molar volume of the vapor, gives

$$\frac{dp}{dT} = \frac{\Delta_{\text{vap}}H_m}{T V_m} \quad (4)$$

For a real gas, the compressibility factor z is given as

$$z = \frac{pV_m}{RT} \quad (5)$$

Solving for the volume of the vapor gives

$$V_m = zRT / p \quad (6)$$

Substituting eq 6 into eq. 4 and rearranging gives

$$\frac{d \ln p}{dT} = \frac{\Delta_{\text{vap}}H_m}{z R T^2} \quad \text{or} \quad \frac{d \ln p}{d 1/T} = \frac{-\Delta_{\text{vap}}H_m}{z R} \quad (7)$$

Assuming that the enthalpy of vaporization is constant over the temperature range of the experiment and integrating eq. 7 gives the Clausius-Clapeyron equation under the assumption that the vapor behaves as a real gas

$$\ln \left(\frac{p_2}{p_1} \right) = \frac{-\Delta_{\text{vap}}H_m}{z R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (8)$$

Therefore, a plot of $\ln p$ versus $1/T$ will yield a straight line of slope $-\Delta_{\text{vap}}H_m / z R$.

The value of z can be determined from standard tables as follows. Experimental measurements of the compressibility factor, z , are difficult near the liquid-vapor coexistence curve. Extrapolation of experimental values to the liquid-vapor coexistence region has been completed, based on the Law of Corresponding States and other theoretical considerations¹. The results for a few substances are shown in Figure 3. The plot is given in terms of the reduced temperature, T_r , where $T_r = T / T_C$, where T_C is the critical temperature of the substance.

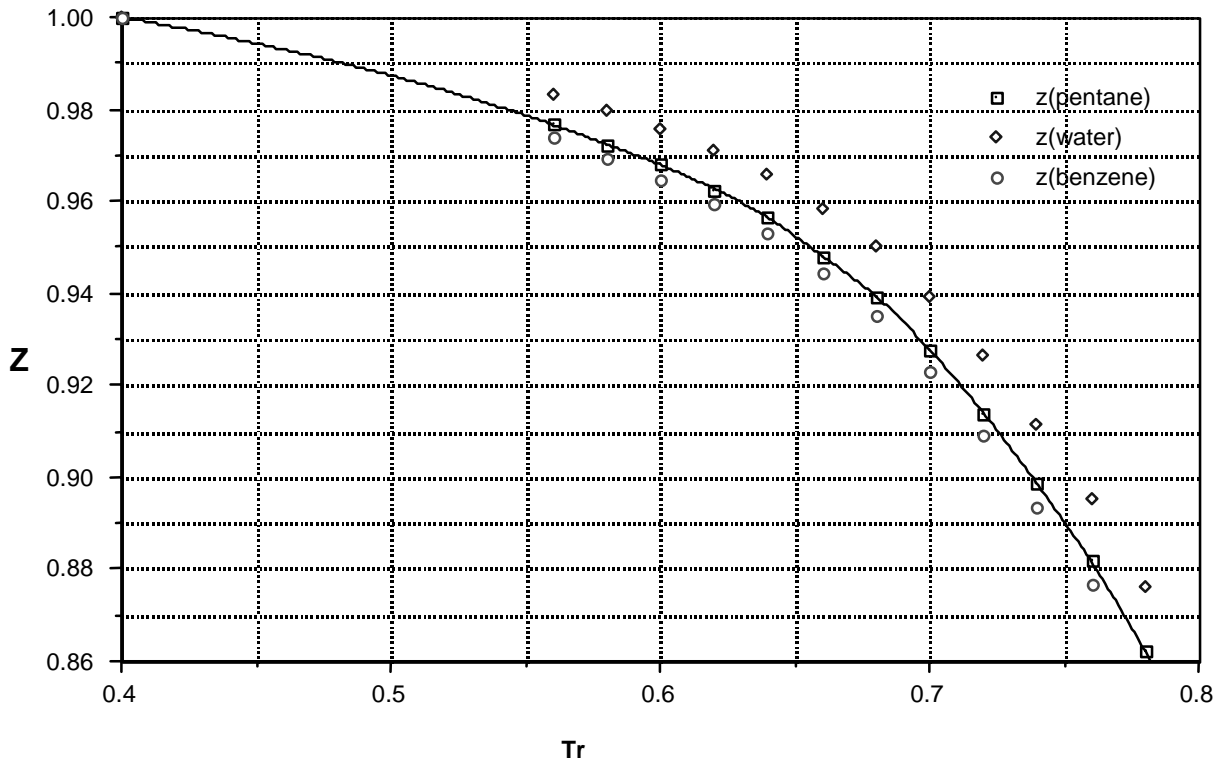


Figure 3. The compressibility factor, z , as a function of reduced temperature along the liquid-vapor coexistence curve. The curves are calculated using tabulated polynomial coefficients from Pitzer, et. al.¹.

Finally, we must consider the effect of the temperature dependence of the enthalpy. Please review in your text that the temperature dependence of the enthalpy of a reaction is

$$\Delta_r H_{T2} = \Delta_r H_{T1} + \Delta_r C_p (T_2 - T_1) \quad (9)$$

where $\Delta_r C_p$ is the difference in heat capacity of products minus reactants. For this *phase transition* the product is the vapor and the reactant is the liquid. If $\Delta_r C_p$ is large, eq. 8 will not hold and the plot of $\ln p$ versus $1/T$ will show some curvature instead of being a straight line.

The entropy of vaporization is also an important quantity. The standard state (1 atm) entropy change can be determined by calculating the enthalpy of vaporization *at the normal boiling point* using eq. 9 and then using eq. 3 at the normal boiling point. However, this calculation gives the entropy change at the normal boiling point, not at 298K as is usually desired. Please review in your text that the temperature dependence of the entropy of a reaction is

$$\Delta_r S_{T2} = \Delta_r S_{T1} + \Delta_r C_p \ln (T_2 / T_1) \quad (10)$$

with $\Delta_r C_p$ as defined above. Eq. 10 can be used to calculate the entropy of vaporization at any temperature (assuming $\Delta_r C_p$ is constant over the temperature range).

Procedure

The vapor pressure curve will be determined by isolating a sample in a vacuum line and measuring the vapor pressure directly on an electronic pressure sensor while changing the temperature using constant temperature baths. The constant temperature baths are "slush" baths made by freezing an organic solvent using liquid nitrogen, LN₂, to produce a "milk shake" consistency slush. Since the slush is an equilibrium mixture of a pure liquid and its solid phase, the bath temperature will be held constant at the normal melting point. Below are listed some common slush baths.

Slush Bath Temperatures (from Dodd and Robinson²)

0°C	water-ice
-22.9°C	carbon tetrachloride
-45.2°C	chlorobenzene
-63.5°C	chloroform
-83.6°C	ethylacetate

The molecular weight of a gas can be determined using its vapor density and the ideal gas law. Vapor density is measured by filling a bulb of known volume and weight with a vapor and determining the weight of the vapor by difference. Knowing the weight of the vapor and the volume, pressure, and temperature allows the calculation of the molecular weight using $PV=nRT$.

Procedure Outline

A diagram of the vacuum line for this experiment is shown in Figure 2. The cold finger is used to protect the vacuum pump. The cold finger is immersed in a dewar of liquid nitrogen, which condenses any vapors so that they don't reach the pump. The circle symbols with X's through

them symbolize stopcocks. The sample is held in the glass sample tube. The gas density bulb is removed for weighing on an analytical balance (however, a mechanical balance must be used so make sure that you know how to use a mechanical analytical balance *before* you come to lab). The pressure sensor is a very accurate ($\pm 0.3\%$) electronic sensor, which has an internal diaphragm that flexes to change the capacitance of the sensor. The capacitance is converted to a corresponding pressure reading by a digital readout. An outline of the procedure is:

1. Evacuate the manifold and immerse the cold finger in LN₂, weigh the evacuated gas density bulb. The exact volume of the bulb is etched in the glass.
2. Fill the sample tube with n-pentane.
3. Freeze the pentane with liquid nitrogen and remove any air from the tube.
4. Immerse the sample tube in a series of slush baths and measure the vapor pressure.
4. At the last temperature fill the gas density bulb with pentane vapor.
5. Determine the weight of the vapor in the gas density bulb.
6. To finish up at the end of the day: evacuate the gas density bulb and manifold.
7. Turn off the pump and remove the cold finger.

Caution:

Don't over-tighten the stopcocks. Close the stopcock until the o-ring appears to "wet" the glass valve seat, then tighten no further. If the stopcock doesn't have o-rings (the valve at the top of the cold trap is of this type), close the stopcock until the teflon appears to "wet" the glass valve seat.

The halogenated hydrocarbons used for slush baths are suspected carcinogens. Always work in the hood and wear gloves when handling these compounds.

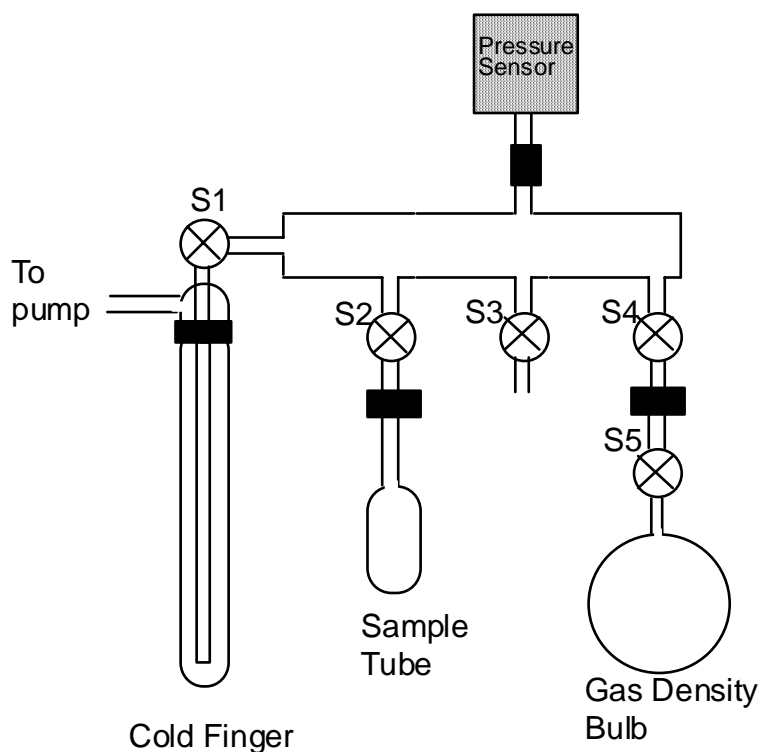


Figure 2. Vacuum line.

Detailed Procedure: Gases behave in a very predictable way-- they expand to fill the accessible space. The detailed directions given below shouldn't replace your common sense about how to do the experiment. Make sure you know what each stopcock does and why you open and close them when you do. You shouldn't need to refer to these directions while you are doing the experiment.

1. Turn on the vacuum pump and pressure sensor at least 3 hours before you begin. The 3 hours is to pump down the vacuum line and to allow the electronics to warm up. Make sure S1, S2, S4, and S5 are open.
2. Close S4 and S5. Remove the gas density bulb and weigh by hanging the bulb from the hook at the top of a mechanical analytical balance. You will have to remove the balance pan to avoid exceeding the weight limit on the balance. Make sure that you know how to use a **mechanical** analytical balance *before* you come to lab.
3. Replace the gas density bulb on the vacuum line and open S4 and S5. Wait for the line to return to 0.0 mmHg pressure.
4. Close S2 and add 3 mL of n-pentane to the sample bulb. Replace the sample bulb on the vacuum line.
5. Using LN₂ freeze the pentane in the sample bulb, then open S2. Freezing the sample keeps the vacuum system from pumping away the liquid while air is being removed from the sample tube.
6. When the pressure returns to 0.0 mmHg close S1 and warm the sample until it thaws.
7. Look up the vapor pressure of n-pentane in the CRC Handbook *before* you come to lab, so that you know how cold the first bath can be. Vapor pressures less than 2 mmHg are difficult to measure on our vacuum line.
8. Prepare the coldest slush bath first. To prepare a slush bath alternately add the slush solvent and LN₂ to a small dewar flask with rapid stirring. Add small amounts of solvent and LN₂ repeatedly to avoid forming a solid mass of frozen solvent. Repeat your additions until you have sufficient slush to cover the sample bulb. The slush should have a milk-shake consistency. If the slush is too thin, all the solid will melt before the sample measurement can be made. If the slush is too thick, the sample tube will break when you move the dewar upwards around the sample. *Always work in the hood and wear gloves when handling these compounds.*
9. Place the first slush bath around the sample. Wait for the pressure to stabilize and record the pressure. Pressure readings should take about 5 minutes to stabilize.
10. Remove the slush bath. Check to make sure that solid remains in the slush. If available, use a platinum resistance thermometer to check the slush bath temperature. If the thermometer isn't set up, just use the table above to determine the temperature. Return the slush bath solvent to its original container for reuse.

11. **Gently** wipe the outside of the sample bulb with a paper towel to avoid contamination of the next slush bath. Go on to the next slush baths. A large beaker of cold water can also be used for temperatures close to room temperature.

12. At the last temperature, you should also do the gas density measurement. To do the density measurement, open S4 and S5 to allow vapor to fill the gas density bulb. After you have recorded the vapor pressure, use a thermometer to measure the air temperature near the gas density bulb (the gas **IN** the density bulb is at room temperature, not at the temperature of the liquid. So you will need the room temperature to calculate the molecular weight). Close S4 and S5 and gently remove the gas density bulb from the vacuum line. Weigh the filled gas density bulb as you did before.

To finish up at the end of the day:

13. Cool the sample bulb with LN₂ to condense all the pentane vapor back into the sample bulb. Close S2.

14. Replace the gas density bulb on the vacuum line. Open S1, S4, and S5 and bring the pressure to 0.0 mmHg.

15. Close S1, turn off the vacuum pump, and unscrew the cold finger. The cold finger won't come all the way off, but the trapped solvents will be able to evaporate anyway.

16. Replace the balance pan on the analytical balance. Replace the solvents in the solvent storage cabinet.

Calculations

Make a plot according to eq. 8. Use the average temperature of your runs to calculate T_r and then read z from Figure 3. Determine $\Delta_{\text{vap}}H_m$ from the slope of your plot and z . This $\Delta_{\text{vap}}H_m$ will correspond to the average temperature of your runs. To calculate $\Delta_{\text{vap}}H_m$ at the normal boiling point, 309.2K, use eq. 9. The heat capacity of gaseous pentane is $120.2 \text{ J mol}^{-1} \text{ K}^{-1}$ (Table 2.11 in Atkins³). The heat capacity of liquid pentane is not available in standard tabulations, but the change in heat capacity for vaporization is a remarkably linear function of the number of carbon atoms, for hexane through decane⁴. The extrapolated value for pentane of $\Delta_{\text{vap}}C_p$ is $-47.26 \text{ J mol}^{-1} \text{ K}^{-1}$. At the normal boiling point, $\Delta_{\text{vap}}H_m = \Delta_{\text{vap}}H_m^\circ$ since the vapor pressure is one atmosphere.

To calculate the standard entropy of vaporization of n-pentane at 298K, use the $\Delta_{\text{vap}}H_m^\circ(309.2\text{K})$ you calculated above and eq. 3 to calculate $\Delta_{\text{vap}}S_m^\circ$ at the normal boiling point. Then use eq. 10 to calculate $\Delta_{\text{vap}}S_m^\circ(298.2\text{K})$.

Use the ideal gas law to determine the molecular weight of pentane from the weight of the vapor in the gas density bulb, the vapor pressure, and the volume and temperature of the gas bulb. Don't be disappointed if your results vary 20% or so from the calculated value. Gas density measurements are expected to give rough estimates only. Note that you don't need to calculate the density of the gas, just use $PV=nRT$ directly.

Make sure to answer the following questions in your discussion:

1. Do you see any evidence that $\Delta_{\text{vap}}H_m$ is temperature dependent over your temperature range?
2. How does your $\Delta_{\text{vap}}S_m^\circ$ compare with other substances? Does n-pentane obey Trouton's rule?
3. If you were able to measure the slush bath temperatures, how close to the tabulated values were the slush bath temperatures? What could cause any discrepancies?
4. Why is $\Delta_{\text{vap}}C_p$ negative?
5. Compare $\Delta_{\text{vap}}H_m^\circ$ to tabulated values. Does the temperature correction in eq. 9 have an important effect?

Literature Cited

1. Pitzer, K. S.; Lippmann, D. Z.; Curl, Jr., R. F.; Huggins, C. M.; and Petersen, D. E., *J. Amer. Chem Soc.*, **1955**, *77*, 3433.
2. Dodd, R. E.; Robinson, P. L. , *Experimental Inorganic Chemistry*, Elsevier Publishing C., Amsterdam, 1957, 56.
3. Atkins, P. W., *Physical Chemistry, 5th Ed.*, Freeman, New York, NY, 1994.
4. Linear extrapolation for the following data derived from Dean, J. A. *Lange's Handbook of Chemistry, 14th Ed.*, McGraw-Hill, Inc., New York, NY, 1992. Table 6.1.:

<u>n-alkane</u>	<u>$\Delta_{\text{vap}}C_{p,m}$ (J mol⁻¹ K⁻¹)</u>
hexane	-52.014
heptane	-58.805
octane	-60.261
nonane	-66.954
decane	-72.785