

Physical Chemistry Laboratory I
CHEM 445
Experiment 6
Vapor Pressure of a Pure Liquid
 (Revised, 01/09/06)

The vapor pressure of a pure liquid is an intensive property of the compound. That is, the vapor pressure of a liquid is independent of the amounts of the two phases as long as both phases are present. This phenomenon is shown in many physical chemistry textbooks in plots of PV isotherms at temperatures below the critical temperature. The horizontal part of the P vs. V isotherm corresponds to the constant vapor pressure of the liquid. The vapor pressure of every liquid is a strongly increasing function of temperature and a very slightly increasing function of applied pressure.

The equation for the variation of vapor pressure of a liquid with temperature is derived in standard texts and often called the Clausius - Clapeyron equation.. Reasonable approximations have been made to achieve this equation.

$$\frac{1}{P} \left(\frac{dP}{dT} \right) = \frac{\overline{\Delta H_{vap}}}{RT^2} \quad (1)$$

In Eq. (1), P is the vapor pressure of the liquid, T is the absolute temperature in K, and $\overline{\Delta H_{vap}}$ is the molar heat of vaporization of the liquid. The vapor pressure of a pure liquid is often represented by Eq. (2), the integrated form of Eq. (1) with the additional assumption that the heat of vaporization is independent of temperature.

$$\ln\{P\} = A - \frac{\overline{\Delta H_{vap}}}{RT} \quad (2)$$

Although the heat of vaporization of a liquid is actually not independent of temperature, Eq. (2) will give an accurate fit to vapor pressure data over a wide range of temperatures, as long as the temperature is well below the critical temperature. There are compensating errors in the approximations.

If very accurate data are obtained or if vapor pressures are obtained over a very wide range of temperatures, then the variation of heat of vaporization with temperature should be considered. The following equation is often used,

$$\overline{\Delta H_{vap}} = a' - b'T \quad (3)$$

Substituting Eq. (3) into equation Eq. (1) and integrating will give a more elaborate equation for vapor pressure as a function of temperature, in which the constants (either positive or negative) are obtained from a fit to the experimental data. This equation (Kirchoff equation) was proposed empirically many years ago to fit accurate vapor pressure data,

$$\ln\{P\} = c + \frac{a}{T} + b \ln\{T\} \quad (4)$$

Other equations have been proposed for the variation of vapor pressure of a liquid with temperature. For the analysis of your data, Eq. (2) is sufficient and $\overline{\Delta H_{vap}}$ is an average molar heat of vaporization over the temperature range.

From standard thermodynamics, $\overline{\Delta H_{\text{vap}}/T}$ = the molar entropy of vaporization. It was observed experimentally and predicted theoretically that this quantity at the normal boiling point would be relatively constant for many non-associated liquids at $\sim 21 \text{ cal/mol}^\circ$ or $\sim 88 \text{ J/mol}^\circ$, Trouton's Rule. [1] Consequently, one may estimate the temperature variation of vapor pressure of a liquid reasonably well near its normal boiling point, simply from the boiling point.

Experimental procedure

You will measure the vapor pressure of methanol.

In this experiment you will use an isoteniscope in a stirred water bath whose temperature you can change relatively easily. The 'system' {see picture} consists of a vacuum pump to reduce pressure, an ice/water cold trap to capture sample vapors, a 3-way stopcock, an isoteniscope (see picture) to contain your sample, a large empty jar (ballast tank) to reduce the pressure fluctuations, and an MKS Baratron to measure the system pressure. A Lauda water bath is provided to control the temperature of the isoteniscope and cyclohexane.

The 3-way stopcock controls pressure changes in the system. If the 3-way stopcock is open to the pump, the pressure is reduced (performed initially to pump down the system). If the 3-way stopcock is opened to the atmosphere, the pressure is increased in the system (performed during heating) and to shut down the system.

IMPORTANT: Before you begin the experiment, check the bath temperature. It should be approximately the same as room temperature. If colder, fine; if much warmer, remove some water and use ice to reduce bath to \sim room temperature.

Remove an isoteniscope from the storage canister and remove the cap. Place the cap in the canister for safe keeping.

Pack some ice around the glass cold trap in the Styrofoam container.

Fill the metal bulb portion $\sim 3/4$ -full with methanol using a Pasteur pipette or a plastic squeeze bottle. The exact amount of liquid is not critical, but the liquid should be clearly visible. When you remove the air, some (much) of the liquid will be lost. No liquid should be in the U-tube portion, although a little is OK as long as the tube is not blocked, because it will evaporate as you reduce the pressure in the system. Slightly tricky manipulation of the isoteniscope is needed to get the liquid into the bulb.

Place the isoteniscope in the constant temperature bath at room temperature and attach the connecting hose to the vacuum system. Turn on the vacuum pump with the 3-way stopcock closed (perpendicular to the gas flow guarantees that the stopcock is closed).

Slowly turn the 3-way stopcock to the vacuum line (color coded) to reduce the pressure in the isoteniscope and the ballast tank. The liquid may boil (bubble) as the pressure is reduced, but it vaporizes even if visible boiling does not occur. You can tell from the sound level of the pump and from the changes in pressure that the vacuum pump is evacuating the system.

Pump on the system for a minute or two. Close the stopcock and let the pressure equilibrate, and note the pressure on the MKS Baratron, which gives a direct reading of the pressure in the ballast tank and the isoteniscope.

Repeat (pump, equilibrate, read) a few times. Remember that when you evaporate a liquid by reducing the pressure, the temperature of the liquid drops and time is needed for the temperature of the liquid in the isoteniscope to equilibrate with the surrounding water bath.

When the pressure no longer changes on evacuating the chamber, the air has been evacuated from the system. Then remove isoteniscope from the bath and tilt the bulb to let

enough liquid into the U-tube portion of the isoteniscope to form a “plug” about halfway up the U-tube. (**Careful: don’t disconnect hose.**) You need liquid in the U-tube of the isoteniscope to verify that the pressure in the isoteniscope and the pressure in the ballast tank are equal.

Allow the isoteniscope to equilibrate in the bath for a few minutes and adjust the pressure in the ballast tank so that the levels of liquid in the two sides of the U-tube are the same. Then, the pressure in the isoteniscope and the pressure in the ballast tank are the same. Record the pressure and bath temperature (± 0.1 °C).

Temperature Effects:

Change the set temperature on the Lauda constant temperature bath by approximately 5 °C. (See directions at the end.) The temperature of the water bath will rise relatively rapidly, perhaps overshoot, and then come to the set value.

As the bath temperature increases, adjust the pressure in the system by allowing **small** amounts of air to enter the system (ballast tank) through the 3-way stopcock. As the temperature increases, the vapor pressure of the liquid increases and the objective is to keep liquid levels approximately equal in the isoteniscope U-tube. When the liquid levels in the two sides of the U-tube are equal, the pressure above the liquid sample in the isoteniscope is the same as the system pressure indicated by the MKS Baratron.

No error results if bubbles of vapor come OUT of the isoteniscope while heating the sample. However, if air leaks into the isoteniscope because you have raised the pressure in the ballast tank too high, your experiment is invalid and must be repeated (after the air has been evacuated from the isoteniscope).

After the temperature has reached a constant value, adjust the pressure in the ballast tank so that the levels of liquid in the U-tube are essentially the same and allow the system to equilibrate for a minute or two. The levels may change a bit because the temperature of methanol in the isoteniscope is still changing slightly. Carefully adjust the pressure in the ballast tank so that the levels are equal and then read and record the temperature (to 0.1 °C) and pressure, to 0.1 mm Hg.

Increase the temperature by another ~ 5 °C and repeat.

Vapor pressure measurements should be continued until system pressure roughly equals atmospheric pressure - around 80 °C. Don’t heat the liquid to cause vapor pressures beyond atmospheric as the system will probably leak.

As in almost all experiments, more than one determination must be made.

It is very difficult to control the temperatures and pressures on cooling without letting air into the isoteniscope. Air will leak into the isoteniscope as the temperature decreases and it is difficult to remove this air with liquid in the U-tube. Consequently, remove the isoteniscope from the bath, let it cool, bring to atmospheric pressure, and remove the rubber tubing. Discard the methanol into the waste container in the hood and refill the isoteniscope. In the initial evacuation procedure, you may have lost a substantial amount of the liquid.

Cool the Lauda water bath to approximately room temperature by passing cold water through the cooling coils and/or adding ice. If you add ice, remove water from the bath with a small beaker to keep the bath from overflowing. Remember to stop the water in the cooling coils before you begin the next heating cycle.

Repeat the heating cycle to determine vapor pressures of methanol at different temperatures. Two “good” sets of data must be obtained.

Clean Up:

To end the experiment:

Turn the stopcock to atmosphere to bring the system to atmospheric pressure.

Switch off the vacuum pump. Turn off the Lauda constant temperature bath.

Remove the isoteniscope from the bath, disconnect the vacuum system hose and replace the cap on the isoteniscope and place the isoteniscope in the storage canister.

Inspect the vacuum pump cold trap: empty any condensate into the waste solvent container in the hood in the adjacent lab. {There is very seldom any. This is not an efficient cold trap.} Empty the ice/water container and reassemble the trap, if necessary. If you cannot disassemble the trap, consult your Laboratory Instructor. Do NOT force disassembly!

Calculations and Discussion:

Present your results in a labeled table, Table 1: P ; $\ln\{P\}$ or $\log\{P\}$; and temperature, both $^{\circ}\text{C}$ and K ; as well as $1/T$, K^{-1} for each experiment. Use a spreadsheet or other data analysis program to analyze and plot your data.

1. Before the second week allowed for the experiment (or at the beginning of lab in the second week), plot P vs. T , either $^{\circ}\text{C}$ or K , Fig. 1 (with an appropriate heading). This is a non-linear plot from which interpolation and extrapolation are difficult; however, this plot will show irregularities in your data easily. Plot P vs. T data for the two experiments with different shapes or colors of symbols on the same figure. If you have done the experiments correctly, the points from the two experiments should be interspersed and one curve should fit both sets of data. If the points do not agree well, do another experiment.

Use Excel (another spreadsheet or data analysis program) to plot and fit your data to a power series or polynomial function (probably second or third order) – a trend line. Show the numerical values of the coefficients in Fig. 1.

The vapor pressures of all liquids increase significantly with increasing temperature. If your data do not show a significant increase with increasing temperature, then you have done the experiment incorrectly.

2. Plot your data in Fig. 2 in the more common form as $\ln\{P\}$ or $\log\{P\}$ vs. $1/T$, according to Eq. (2). Use different shapes or colors for the points for the different experiments. Obtain values for the two constants in this equation (Excel trend line OK). Give values for the coefficients in Fig. 2.

If the experiment is done correctly and the data are analyzed correctly, the plot should be a “reasonably” straight line and the two sets of data should describe a single curve.

3. In analyzing data, one should always examine the differences between the observed and calculated values for systematic variations. In Table 2 list T , $P\{\text{Exp}\}$, $P\{\text{calc, Eq. (2)}\}$, $\{P(\text{Exp}) - P(\text{Calc})\}$ and $\{P(\text{Exp}) - P(\text{Calc})\}/P(\text{Exp})\}$. In Fig. 3, plot the fractional difference between the observed and “fitted” data, $\{P(\text{Exp}) - P(\text{Calc})\}/P(\text{Exp})\}$ vs. T . Note any systematic variation.

4. As you do for all experiments, compare your results with literature values: for vapor pressures and for the molar heat of vaporization of methanol. Give reference(s) for your values. Compare your values of $\Delta H_{\text{vap}}/T_{\text{nbp}}$ with Trouton’s Rule values (given earlier in this experiment). Use your equation for $\ln\{P\}$ or $\log\{P\}$ vs $1/T$ to calculate the normal boiling point of methanol. Compare your value with literature value(s).

Analyze the following set of data {Boublik, Fried, Hala, *The Vapor Pressures of Pure Substances*, Elsevier, 1984} as you analyzed your data: plots of P vs. T, $\ln\{P\}$ or $\log\{P\}$ vs. $1/T$, $\{P(\text{Exp}) - P(\text{Calc})\}/P(\text{Exp})$ vs. T, and calculate nbp, ΔH_{vap} from Eq. (2). These are data for the vapor pressure for another compound and are clearly not the same as your data.

t, °C	15.00	15.00	19.99	20.01	25.00	30.00	35.00
P, mm Hg	74.1	74.2	97.5	97.7	127.2	164.1	209.8
t, °C	40.00	45.00	49.99	54.99	59.99	64.50	
P, mm Hg	266.0	334.4	417.0	516.2	634.4	759.5	

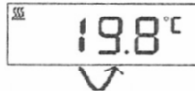
References

1. S. Glasstone, *Textbook of Physical Chemistry*, 2nd Ed., D. van Nostrand Co., New York, 1946

6.3 Setpoint selection



or



– Shortly press one of these keys → adjusted setpoint appears for approx. 4 s.

– °C is flashing, in contrast to the actual value.

– During the 4 s. start to set the required setpoint using the keys.

– Speeding the setting process by:

a) continuous pressing the keys or

b) pressing one key (holding it down) and shortly pressing the other key.

– Briefly releasing (1 s) the key (s) and again pressing one of the keys moves the cursor one place to the right.

– Display flashes 4 s → the new value is accepted automatically, or

– Value is entered immediately with this key.

– For safety reasons the setpoint can only be adjusted up to 2 °C above the upper limit of the operating temperature range of the particular unit type