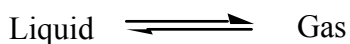


## Vapor Pressure and Heat of Vaporization

When a sample of a liquid is introduced into a container, the liquid will tend to evaporate. Molecules will escape from the relative confinement of the liquid state into the gaseous state. If the container is closed, this conversion will appear to stop when equilibrium is achieved. Under equilibrium conditions, the rate of evaporation equals the rate of condensation.



A measure of the extent of vaporization is the vapor pressure—the partial pressure exerted by the gas phase in equilibrium with the liquid phase. Other gases, e.g. air, can be present, but what matters here is the pressure of the substance involved in the gas-liquid equilibrium. Vapor pressure can be expressed in any convenient unit—mm Hg (torr), atmospheres, bars, pascals, kilopascals, etc. The higher the vapor pressure of a substance, the greater the concentration of the compound in the gaseous phase and the greater the extent of vaporization. Liquids vary considerably in their vapor pressures. If two substances are compared at the same temperature, the more volatile one will have the higher vapor pressure.

You know from experience that increasing the temperature can increase the extent of evaporation of a liquid. Indeed, vapor pressure increases with increasing temperature. When the vapor pressure equals the atmospheric pressure, bubbles of vapor form and escape. This temperature is defined as the normal boiling point.

In this experiment you will measure the vapor pressure of a liquid at a variety of temperatures. You will find that a plot of the vapor pressure ( $p$ ) versus temperature ( $T$ ) is not a straight line. The vapor pressure increases more rapidly than the temperature. However, it is possible to obtain a straight line by making use of equation (1).

$$\ln p = -\Delta H_{\text{vap}}/RT + C \quad (1)$$

In equation (1),  $\ln p$  indicates the natural logarithm (base  $e$ ) of the vapor pressure,  $\Delta H_{\text{vap}}$  is the heat of vaporization of the compound,  $R$  is the gas constant (8.314 J/mole K), and  $T$  is the equilibrium temperature (in Kelvin) corresponding to vapor pressure  $p$ . You don't need to worry about  $C$ , a constant of integration. Note that the variables you will be measuring in this experiment are  $p$  and  $T$ . Equation (1) should yield a straight line if  $\ln p$  is plotted along the vertical ( $y$ ) axis and  $1/T$  is plotted along the horizontal ( $x$ ) axis. The slope of this line,  $d(\ln p)/d(1/T)$  equals  $-\Delta H_{\text{vap}}/R$ . Thus, if a numerical value of the slope is obtained from the graph of your experimental data, you should be able to calculate a value for  $\Delta H_{\text{vap}}$ . The heat of vaporization represents the amount of thermal energy necessary to convert one mole of the liquid in question into the gaseous state. It is usually reported in kJ/mol.

## Advance Study Assignment

1. The vapor pressure of acetone at 20°C is 185.5 mm Hg, and the vapor pressure of water at this same temperature is 17.5 mm Hg. Predict which of the two liquids will have a higher normal boiling point and explain why.
2. Provide a molecular explanation that accounts for the differences in the vapor pressures and boiling points of water and acetone.
3. Sketch the appearance of a plot of  $\ln p$  vs  $1/T$ .

## Experimental Procedure

In this experiment you will measure vapor pressure as a function of temperature, using a digital gas pressure sensor interfaced with a Vernier LabPro and a TI graphing calculator. The apparatus is pictured in Figure 1. A 125 mL suction flask is fitted with a two-hole rubber stopper. The pressure sensor is attached via a plastic tube to a special fitting in one of the holes in the stopper. Passing through the other hole in the stopper is one end of a piece of straight glass tubing fitted with a Teflon stopcock. The glass tubing has an 8 mm outside diameter with the stopcock midway along its 30 cm length. This tube will be used to introduce the liquid being studied into the flask.

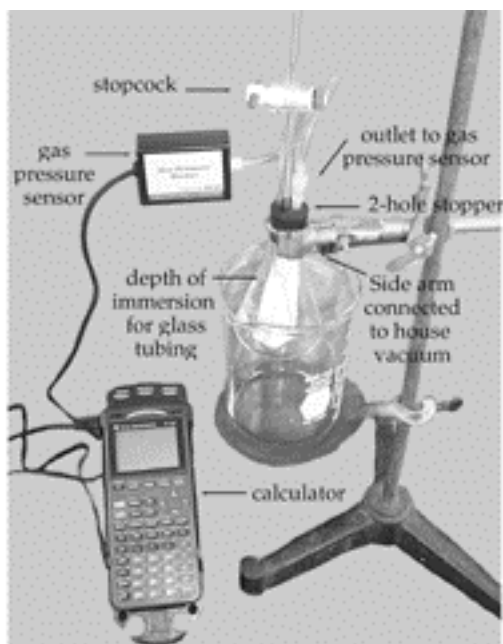


Figure 1: Experiment Apparatus

Place a piece of clean filter paper into the clean and dry flask. The purpose of the paper is to absorb the liquid and facilitate the establishment of equilibrium. Fit the rubber stopper tightly into the flask and make sure the stopcock is closed. Attach the side arm of the flask to an aspirator, house vacuum port, vacuum line, or vacuum pump using heavy walled rubber tubing. Partially evacuate the flask until the pressure sensor reads about 10 kPa. Close off the rubber tubing on the side arm with a pinch clamp. Place the flask in a beaker containing ice and water. This will be your constant temperature bath. Allow the apparatus to come to thermal equilibrium. When the temperature and pressure are constant (the former at or near 0°C) read and record the values of both. Use a pipette to transfer approximately 2 mL of your liquid to the sample-delivery tube. It is not necessary to measure the exact amount (why not?), but this volume will come close to filling the tube above the stopcock and will not all vaporize when introduced into the flask. Introduce the liquid by opening the stopcock,

but close the stopcock before the liquid level drops below the stopcock and air is introduced into the system.

Monitor the pressure; when it reaches a constant value, record that value and the corresponding temperature. Without changing the flask or its connections, increase the temperature of the water bath to about 10°C. When the temperature and pressure stabilize, read and record both. Repeat temperature and pressure readings at roughly 20°C, 30°C, 40°C and 50°C. At this point you can disassemble the apparatus, remove the filter paper, and clean and dry the flask. The apparatus is then ready for a repeat trial on your original liquid or for a series of measurements on a new sample.

In processing your data, you need to take into consideration that you started the experiment with some air in your flask. Hence, the pressure that you read after you introduced your liquid is the sum of the pressure of the air originally present and the vapor pressure of the sample. For a first approximation, assume that the pressure of the air remains constant at all temperatures and is equal to the pressure measured at 0°C before the introduction of the unknown. This assumption and your raw data will permit you to calculate the vapor pressure for each temperature at which a measurement was made. Enter your data in a spreadsheet and use the graphing program to plot vapor pressure vs. absolute temperature. Then calculate  $\ln p$  and  $1/T$  for each set of measurements and plot these two variables to examine the relationship specified in equation (1), fitting the data with the best straight line. The equation of this line should yield the slope, from which you can calculate a value for the heat of vaporization. The equation also permits you to calculate the temperature at which the vapor pressure equals 1 atm, i.e. the normal boiling point.

On reflection, you should recognize that the method of treating the data described in the previous paragraph makes an over simplification. The pressure of the air in the flask does not remain constant as the temperature increases, even if the system doesn't leak. (Does it increase or decrease?) Your knowledge of the properties of ideal gases should enable you to calculate the pressure of the air at each temperature, and hence obtain more accurate values for the vapor pressure. It is your assignment to devise a strategy for making this correction and to refine your calculation. Then use your new results to plot  $p$  vs.  $T$  and  $\ln p$  vs.  $1/T$ , determine the equation of the straight line, and calculate the heat of vaporization and the normal boiling point.

Your report should include your raw pressure and temperature data, sample calculations, and an explanation of how you made the correction described in the previous paragraph. Your spreadsheets and graphs are important parts of your report, as are your final results. If you know the identity of your liquid, look up accepted values for the heat of vaporization and normal boiling point and compare these results with your own. Discuss the cause and nature of any errors.