A Simple Experiment for Determining Vapor Pressure and Enthalpy of Vaporization of Water

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The concept of vapor pressures of liquids is discussed in most general chemistry courses. The Clausius-Clapeyron equation is introduced as a means of describing the variation of vapor pressure with temperature and for determining enthalpy of vaporization. Normally, the subject is treated only in the lecture portion of the course because experiments to measure vapor pressure as a function of temperature are not suitable for freshman chemistry laboratories. It is possible, however, using the simplest of laboratory equipment to determine the vapor pressure of water in the range 50°C to 80°C. Only a tall beaker, a graduated cylinder, and a thermometer are required.

Although the apparatus is quite different, the method operates on the same principle as an experiment first developed by Borrell and Nyburg. However, their apparatus is not as simple as the one proposed here and requires use of liquid mercury. The present experimental method is particularly well suited for the freshman chemistry laboratory.

Method

A sample of air is trapped in an inverted 10-ml graduated cylinder immersed in a beaker of water. The water is heated to about 80°C, and the trapped gas becomes saturated with water vapor rapidly at this temperature. The temperature of the water bath and the volume of gas are recorded. The bath is then cooled and the readings of temperature and gas volume are taken at intervals of 5°C or less. The number of moles of water in the gas phase changes with temperature, but the amount of air is constant.

With knowledge of the moles of air in the gas sample, the partial pressure of air can be calculated at each temperature, and the vapor pressure of water can be obtained by determining the difference from the barometric pressure. The number of moles of air in the mixture can be found from measurements of volume, temperature, and pressure at a temperature near 0°C, where the water content of the gas is less than 1% and is neglected. The enthalpy of vaporization is calculated through the Clausius-Clapeyron equation from a plot of the logarithm of the vapor pressure versus 1/T.

There is a small systematic error resulting from the use of inverted graduated cylinders because the meniscus at the gas-water interface is reversed. See the figure. It has been estimated, by introducing known volumes of air into a completely filled inverted cylinder, that the error involved with use of our 10-ml graduated cylinders is 0.2 ml. Then this value is subtracted as a correction to each volume reading.

Procedure

1) Fill a 10-ml graduated cylinder about 2/3 full with distilled water. Cover the top with a finger and quickly invert and lower the cylinder into a tall beaker that has been filled with water. An air sample of 4 to 5 ml should be trapped within the cylinder.
2) Add more water if necessary to the beaker to ensure that the trapped air is surrounded by water. Then heat with a Bunsen burner to approximately 80°C.
3) Observe the volume of trapped air. When it expands beyond the scale on the cylinder, remove the burner and allow the water to cool. When the gas begins to contract and the volume can again be read, read and record the volume to the closest 0.1 ml and the temperature of the water to the nearest 0.1°C. Stir the water bath frequently to avoid thermal gradients.
4) Carefully take the water bath to a tray on the bench top. As the water cools, make additional measurements at approximately 5°C intervals down to 50°C. Ice may be added to speed the cooling; any overflow from the bath will be trapped in the tray below the beaker.
5) After the temperature has reached 50°C, cool the water rapidly to less than 5°C by adding ice. Record the gas volume and the water temperature.
6) Obtain a reading of the atmospheric pressure.

Calculations

1) Correct all volume readings by subtracting 0.3 ml to compensate for the inverted meniscus. Using the measured values for volume and temperature from step 5 and the atmospheric pressure, calculate the number of moles of trapped air. Assume that the vapor pressure of water is negligible compared to atmospheric pressure at the low temperature.
2) For each temperature, calculate the partial pressure of air in the gas mixture.

\[ \rho_{\text{air}} = \frac{n_{\text{air}} RT}{V} \]

3) Calculate the vapor pressure of water at each temperature.

\[ \rho_{\text{H}_2\text{O}} = \rho_{\text{atm}} - \rho_{\text{air}} \]

(An optional, small correction may be made by correcting for the pressure effect of the difference in water levels.)
4) Plot \( \log \rho_{\text{H}_2\text{O}} \) versus 1/T, and draw the best straight line through the points. Determine the slope, and using the Clausius-Clapeyron equation, calculate \( \Delta H_{\text{vap}} \). Find the value of the vapor pressure of water at 65°C using the graph.

Results

Freshman students in the first-semester general chemistry course at City College of San Francisco obtain results very close to the literature values. Averaging the results of 55 students gave a mean value of \( \Delta H_{\text{vap}} \) of 9.9 kcal/mole, which is close to the value, 10.2 kcal/mole obtained using a least-squares fit of literature values of the vapor pressure of water between 50°C and 80°C to the Clausius-Clapeyron equation. The standard deviation of 1.8 kcal/mole reflects the

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1 Borrel, P., and Nyburg, S.C., J. CHEM. EDUC., 42, 551 (1965)
experimental uncertainties in readings plus plotting and
drawing the best line through experimental points. The av-
erage value of the vapor pressure at 65° read from the graph
was 188.4 torr, a value in excellent agreement with the hand-
book value of 187.5 torr, but the standard deviation of 44 torr
shows a rather wide scatter in the results. An examination of
the students' data showed that about half the scatter, as
measured by both the standard deviations given above, re-
sulted from the imprecise graphing procedures of freshman
students who have had only limited experience in estimating
best lines through data points.

Several refinements are possible to extend or improve the
experiment, while still maintaining simplicity. Accuracy and
precision of the volume readings could be improved by sub-
stituting a gas measuring tube for the graduated cylinder. The
extrapolation procedure of Borrell and Nyburg could be used
to establish that the vapor pressure of water is indeed negli-
gible around 5°C.

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