EXPERIMENT 18. VAPOR PRESSURE OF A PURE LIQUID

When a pure liquid is placed in an evacuated bulb, molecules will leave the liquid phase and enter the gas phase until the pressure of the vapor in the bulb reaches a definite value that is determined by the nature of the liquid and its temperature. This pressure is called the vapor pressure of the liquid at a given temperature. The equilibrium vapor pressure is independent of the quantity of liquid and vapor present as long as both phases exist in equilibrium with each other at the specified temperature. As the temperature is increased, the vapor pressure also increases up to the critical point, at which the two-phase system becomes a homogeneous, one-phase fluid.

If the pressure above the liquid is maintained at a fixed value (say by admitting air to the bulb containing the liquid), then the liquid may be heated up to a temperature at which the vapor pressure is equal to the external pressure. At this point, vaporization will occur by the formation of bubbles in the interior of the liquid as well as at the surface; this is the boiling point of the liquid at the specified external pressure. Clearly the temperature of the boiling point is a function of the external pressure; in fact, the variation of the boiling point with external pressure is seen to be identical with the variation of the vapor pressure with temperature.

In this experiment the variation of vapor pressure with temperature will be measured and used to determine the molar heat of vaporization.

THEORY

We are concerned here with the equilibrium between a pure liquid and its vapor:

\[ X(l) = X(g) \quad (p, T) \]  

(1)

It can be shown thermodynamically that a definite relationship exists between the values of \( p \) and \( T \) at equilibrium as given by

\[ \frac{dp}{dT} = \frac{\Delta S}{\Delta V} \]  

(2)

In Eq. (2) \( dp \) and \( dT \) refer to infinitesimal changes in \( p \) and \( T \) for an equilibrium system composed of a pure substance with both phases always present; \( \Delta S \) and \( \Delta V \) refer to the change in \( S \) and \( V \) when one phase transforms to the other at constant \( p \) and \( T \). Since the change in state (1) is isothermal and \( \Delta G \) is zero, \( \Delta S \) may be replaced by \( \Delta H / T \). The result is

\[ \frac{dp}{dT} = \frac{\Delta H}{T\Delta V} \]  

(3)

Equation (2) or (3) is known as the Clapeyron equation. It is an exact expression which may be applied to phase equilibria of all kinds although it has been presented here in terms of the one-component liquid-vapor case. Since the heat of vaporization \( \Delta H_v \) is positive and \( \Delta V \) is positive for vaporization, it is seen immediately that vapor pressure must increase with increasing temperature.

For the case of vapor-liquid equilibria in the range of vapor pressures less than 1 atm, one may assume that the molal volume of the liquid \( \tilde{V}_l \) is negligible in comparison with that of the gas \( \tilde{V}_g \), so that \( \Delta V = \tilde{V}_g \). This assumption is very good in the low-pressure region, since \( V_l \) is usually only a few tenths of a percent of \( V_g \). Thus we obtain
\[ \frac{dp}{dT} = \frac{\Delta \tilde{H}_v}{TV_g} \]  

(4)

Since \( d\ln p = dp/p \) and \( d(l/T) = -dT/T^2 \), we can rewrite Eq. (4) in the form.

\[ \frac{d \ln p}{d(1/T)} = -\frac{\Delta \tilde{H}_v}{R} \frac{RT}{p\tilde{V}_g} = -\frac{\Delta \tilde{H}_v}{Rz} \]  

(5)

where we have introduced a compressibility factor \( z \) for the vapor:

\[ z = \frac{p\tilde{V}_g}{RT} \]  

(6)

Equation (5) is a convenient form of the Clapeyron equation. We can see that if the vapor were a perfect gas (\( z = 1 \)) and \( \Delta \tilde{H}_v \) were independent of temperature, then a plot of \( \ln p \) versus \( \ln T \) would be a straight line the slope of which would determine \( \Delta \tilde{H}_v \). Indeed, for many liquids \( \ln p \) is almost a linear function of \( 1/T \), which implies at least that \( \Delta \tilde{H}_v/z \) is almost constant.

![Figure 1](image)

**FIGURE 1**

The compressibility factor \( z \) of saturated vapor as a function of reduced temperature \( T_r \) for water, benzene, and n-heptane.

Let us now consider the question of gas imperfections, i.e., the behavior of \( z \) as a function of temperature for the saturated vapor. It is difficult to carry out \( p-V-T \) measurements on gases close to condensation and such data are scarce, but data are available for water, and theoretical extrapolations have been made for the vapor of "normal" liquids based on data obtained at higher temperatures. Figure 1 shows the variation of the compressibility factor \( z \) for a saturated vapor as a function of temperature in the case of water and two normal liquids, benzene and n-heptane. For the temperature axis, a "reduced" temperature \( T_r \) is used; \( T_r = T/T_c \), where, \( T_c \) is the critical temperature. This has the effect of almost superimposing the curves of many different substances; indeed, by the law of corresponding states such curves would be exactly
superimposed. In general, it is clear that $z$ decreases as the temperature increases. Water, due to its high critical temperature, is a reasonably ideal gas even at 100 °C where $z$ equals 0.986. But n-heptane at its 1-atm boiling point of 98 °C has a value of $z$ equal to 0.95 and is relatively non-ideal. For many substances, sizable gas imperfections are present even at pressures below 1 atm.

Next we must consider variation of $\Delta H_v$ with temperature. For a change in state such as Eq. (1)

$$
\Delta H_{T_2} = \Delta H_{T_1} + \int_{T_1}^{T_2} \Delta C_p \, dT + \int_{p_1}^{p_2} \left( \frac{\partial \Delta H}{\partial p} \right)_T \, dp
$$

(7)

Since the final term is zero for a perfect gas and small for most real gases, it is possible to approximate Eq. (7) by

$$
\Delta H_{T_2} \approx \Delta H_{T_1} + \Delta C_p(T_2 - T_1)
$$

(8)

where the average value over the temperature interval, $\Delta C_p$, is used. For $\Delta H_v$ to be independent of temperature, $\Delta C_p$ must be very close to zero, which is generally not true. Heat capacities for water, benzene, and n-heptane are given below as typical examples.4,5 For n-heptane, the specific heat of both gas and liquid changes rapidly with temperature; use of average values will give only an order-of-magnitude result. In general, the value of $\Delta H_v$ will decrease as the temperature increases.

<table>
<thead>
<tr>
<th>Compound</th>
<th>T Range (°C)</th>
<th>$\bar{C}_p$ (g)</th>
<th>$\bar{C}_p$ (l)</th>
<th>$\Delta \bar{C}_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>25 – 100</td>
<td>8</td>
<td>18</td>
<td>-10</td>
</tr>
<tr>
<td>Benzene</td>
<td>25 – 80</td>
<td>22</td>
<td>35</td>
<td>-13</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>25 – 100</td>
<td>\text{~}47</td>
<td>\text{~}58</td>
<td>-11</td>
</tr>
</tbody>
</table>

Since both $\Delta H_v$ and $z$ decrease with increasing temperature, it is possible to see why $\Delta H_v/z$ might be almost constant and give a nearly linear plot of $\ln p$ versus $1/T$.

METHODS

There are several experimental methods of measuring the vapor pressure as a function of temperature.6 In the gas-saturation method a known volume of an inert gas is bubbled slowly through the liquid, which is kept at constant temperature in a thermostat. The vapor pressure is calculated from a determination of the amount of vapor contained in the outcoming gas or from the loss in weight of the liquid. A common static method makes use of an isoteniscope, a bulb with a short U tube attached. The liquid is placed in the bulb, and some liquid is placed in the U tube. When the liquid is boiled under reduced pressure, all air is swept out of the bulb. The isoteniscope is then placed in a thermostat. At a given temperature the external pressure is adjusted so that both arms of the U tube are at the same height. At this setting, the external pressure, which is equal to the pressure of the vapor in the isoteniscope, is measured with a mercury manometer. A common dynamic method is one in which the variation of the boiling point with external applied pressure is measured. The total pressure above the liquid can be varied and maintained at a given value by use of a large-volume ballast bulb; this pressure is then measured with a mercury manometer. The liquid to be studied is heated until boiling occurs, and the temperature of the refluxing vapor is measured in order to avoid any effects of
superheating. The experimental procedure for both the isoteniscope and a boiling point method is given below.

EXPERIMENTAL

1 Boiling-point method

The apparatus should be assembled as shown in Fig. 2. A Claissen distilling flask can be used in this experiment by closing off the side arm with a rubber policeman. Use pressure tubing for connecting the condenser and the manometer to the ballast bulb. Fill the flask about one-third full (just above the level of the baffle) with the liquid to be studied. A few Carborundum boiling chips should be added to reduce "bumping." Be sure that the thermometer scale is visible over a range of at least 50 °C below the boiling point at 1 atm. Heating should be accomplished with either a bunsen burner or an electrical heating mantle placed directly below the flask F. The baffle is used to prevent superheating of the vapor.
Use the manometer with the greatest care; be careful not to allow liquid to condense in it. Stopcock \( X \) should be open only when the manometer is to be read and closed immediately after each reading. Stopcock \( X \) should not be open at the same time as stopcock \( S \) is open, either to vacuum or to the air.

To make a reading, adjust the heating so as to attain steady boiling of the liquid, but avoid heating too strongly. Preferably, heat the flask at a point an inch or so to one side of center. When conditions appear to be steady, open stopcock \( X \) carefully and watch the manometer. When manometer and thermometer appear to be as steady as they can be maintained, read them as nearly simultaneously as possible. The thermometer scale should be read to the nearest 0.1 °C, and vapor should be condensing on and dripping from the thermometer bulb to ensure that the equilibrium temperature is obtained. In reading the manometer, record the position of each meniscus (\( h_1 \) and \( h_2 \)), keeping your line of sight level with the meniscus to avoid parallax error. Estimate your readings to the nearest 0.1 mm. Record the ambient air temperature at the manometer several times during the run.

To change the pressure in the system between measurements, first remove the heater, then check to make sure that stopcock \( X \) is closed. After a short time admit some air or remove some air by opening stopcock \( S \) for a few seconds. Be especially careful in removing air from the ballast bulb to avoid strong bumping. Then open stopcock \( X \) carefully to measure the pressure on the manometer. Repeat as often as necessary to attain the desired pressure. Close stopcock \( X \) and restore the heater to its position under the flask.

Take readings at approximately the following pressures:
- Pressure descending: 760, 600, 450, 350, 260, 200, 160, 130, 100, 80 Torr
- Pressure ascending: 90, 110, 140, 180, 230, 300, 400, 520, 670 Torr

2 Isoteniscope method

In this technique much of the equipment shown in Fig. 2 is used, but the distilling flask and reflux condenser are replaced by an isoteniscope mounted in a glass thermostat as shown in Fig. 3. The heater is operated from a Variac voltage control, and the water bath should be vigorously stirred to ensure thermal equilibrium. The liquid to be studied is placed in the isoteniscope so that the bulb is about two-thirds full and there is no liquid in the U tube. Then the isoteniscope is placed in the thermostat (which should be at room-temperature) and is connected to the ballast bulb and manometer (which are assembled and connected as in Fig. 2).

Air is swept out of the bulb by cautiously and slowly reducing the pressure in the ballast bulb until the liquid boils very gently. Continue pumping for about 4 min, but be careful to avoid evaporating too much of the liquid. Then tilt the isoteniscope so that some liquid from the bulb is transferred into the U tube. Carefully admit air to the ballast bulb through stopcock \( S \) until the levels of the liquid in both arms of the U tube are the same. Read and record the temperature and the pressure on the mercury manometer. (The procedure for operating and reading this manometer is described in Section 1.) To establish that all the air has been removed from the isoteniscope, cautiously reduce the pressure in the ballast bulb until a few bubbles are observed passing through the U-tube liquid. Then determine the equilibrium pressure reading. Repeat the above procedure, if necessary, until successive vapor-pressure readings are in good agreement.

Once the air is removed and a good pressure reading at room temperature is obtained, heat the thermostat bath to a new temperature about 5°C above room temperature. Keep the liquid levels in the U tube approximately equal at all times. When the bath temperature is steady at its
new value, adjust the pressure in the ballast bulb until the levels in the U tube are equal and record both temperature and pressure.

FIGURE 3
Isoteniscope: (a) Schematic diagram of the apparatus which must be connected to the ballast bulb and manometer shown in Fig. 2; (b) an alternate design for the isoteniscope. (An even more elaborate type of isoteniscope is described by Arm et al.)
Take readings at approximately 5 °C intervals until the bath is at about 75 °C, and then take readings at decreasing temperatures that are between the values obtained on heating.

**CALCULATIONS**

Correct all manometer pressure readings \((h_2 - h_1)\) for the fact that the mercury is not at 0 °C by multiplying by \((1 - 1.8 \times 10^{-4} t)\), where \(t\) is the Celsius temperature of the manometer. If \(t\) has been reasonably constant during the experiment, use an average value and apply the same correction factor to all pressures.

Convert all Celsius temperature readings to absolute temperatures \(T\) and plot \(\log_{10} p\) versus \(1/T\). If there is no systematic curvature, draw the best straight line through the points. If there is noticeable curvature, draw a smooth curve through the points and also draw a straight line tangent to the curve at about the midpoint.

Determine the slope of the straight line or tangent. From Eq. (5) it follows that this slope is \(-\Delta H_v/2.303Rz\). Estimate the value of \(z\) for the saturated vapor at the appropriate temperature from Fig. 1 and calculate \(\Delta H_v\) in calories per mole. Report the value of the heat of vaporization and of the vapor pressure for the liquid together with the applicable temperature (corresponding to the midpoint of the range studied).

**DISCUSSION**

Using Fig. 1 and Eq. (8), estimate the variation in \(\Delta H_v/\ln z\) over the range of temperatures studied. Indicate clearly whether \(\Delta H_v/\ln z\) should increase or decrease with increasing temperature. Does your \(\log_{10} p\) versus \(1/T\) plot show a curvature of the correct sign? Evaluate a quantitative uncertainty in your value of \(\Delta H_v/\ln z\) by the method of "limiting slopes." Comment on this uncertainty in relation to the variation with temperature calculated above. Discuss possible systematic sources of error.

**REFERENCES**

1. Any standard text on chemical thermodynamics, such as F. T. Wall, "Chemical Thermodynamics," 2d ed., Freeman, San Francisco (1965).