Experiment 2

VAPOUR PRESSURE OF A PURE SUBSTANCE

The equilibrium vapor pressure of solid and liquid benzene will be measured over a sufficient temperature range to allow evaluation of the heats of sublimation and vaporization. Two techniques will be used: the static method and the isoteniscope.

Theory

If the heat of vaporization of a liquid is assumed to be constant over the temperature range of interest, integration of the Clausius-Clapeyron equation gives a simple form to the temperature dependence of the vapor pressure.

\[ \ln P = -\frac{\Delta H_{\text{vap}}}{RT} + \text{constant} \]

Actually, the heat of vaporization of benzene decreases by about 4 kJ/mol going from the melting point (5.533°C) to the normal boiling point (80.100°C). Therefore, when one plots lnP versus 1/T and draws the best straight line through the data points, the slope will be characteristic of an average heat of vaporization over the temperature range of measurement. In average heat of sublimation may be obtained in the same way. The relation with the heat of fusion \( \Delta H_{\text{sub}} = \Delta H_{\text{fus}} + \Delta H_{\text{vap}} \), is exact only when the values at the triple point are used. We will use this relation only to get an approximate heat of fusion from the average heats of sublimation and vaporization derived from vapor pressure measurements.

The Static Method

In this method the equilibrium vapor above the condensed phase is in direct contact in an evacuated system with a mercury U-tube manometer. The temperature of the condensed phase is controlled by immersing the sample bulb in a bath. The rest of the apparatus must be above the bath temperature to prevent distillation. Hence this method can only be used below room temperature.

Experimental Procedure

The measurement of vapor pressure appears deceptively simple. It is surprisingly difficult to get accurate results. Attention to temperature control and thermal equilibration is important. In principle one could measure vapor pressures above room temperature by refluxing the sample against an atmosphere of air of varying pressure. In practice rapid boiling
is always accompanied by superheating. To circumvent this problem we use the apparatus shown below.

The isoteniscope is immersed in a temperature controlled water bath. The benzene sample is added to volumes A and B of the isoteniscope. With the vacuum pump (located under the nearby fume hood) turned on, the air pressure in the entire apparatus can be controlled by either letting in air through one valve or pumping air out the other valve.

As the temperature is equilibrating to the first setpoint, the space between A and B is purged of air by lowering the pressure until gentle bubbling occurs through U-tube B. The vapor should not reflux much above the o-ring joint that connects the isoteniscope to the manifold. After the temperature has reached a steady reading, the pressure is adjusted until the liquid levels on both sides of the U-tube are equal. At this point the vapor pressure of the pure sample between A and B is equal to the pressure of air + benzene in the rest of the apparatus. The pressure is monitored using an MKS capacitance manometer. The purging/pressure adjustment cycle should be repeated until a consistent result is obtained, indicating that the volume between A and B has indeed been purged of air. Then the experiment is repeated at the next temperature. The vapor pressure of benzene should be measured in the isoteniscope at precisely measured temperatures near 30°C, 50°C, and 70°C. One series of measurements is made with increasing temperature and another with decreasing temperature. The temperature setpoints can be different when the temperature is lowered.

The vapor pressure of benzene should be measured in the static apparatus at several temperatures between about –5°C and 20°C. A bath of alcohol cooled by dropping bits of
dry-ice in it may be used or, alternately, a refrigerated circulation bath may be provided. If the dry ice cooled bath is used it should be stirred well to achieve a uniform temperature. Measure the temperature to 0.1 with the thermometer as close to the sample as possible. Measure the vapor pressure to 0.2 mm Hg (torr). The benzene must be completely melted before points can be taken above the melting point.

There is great merit in plotting the data as it is taken (as lnP vs. 1/T). Semilogarithmic graph paper is very useful in this regard. After the static run and the first isoteniscope run any regions of suspect data will be apparent. Then concentrate the second isoteniscope run on these regions, and repeat the static run if necessary.

**Treatment of Data**

Plot lnP versus 1/T (all runs on one graph!). Mark the melting point. Now draw two "best" straight lines through the data points for the solid and liquid respectively, such that they intersect at the melting point. A computer program may be available in the lab which does this fit. Calculate the heats of sublimation, vaporization, and fusion in kJ/mol.

**Illustrative Problem**

From the following values of the vapor pressure of water, calculate the heats of sublimation, vaporization, and fusion.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Vapor Pressure (torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-20°C</td>
<td>0.776</td>
</tr>
<tr>
<td>0°C</td>
<td>4.58</td>
</tr>
<tr>
<td>20°C</td>
<td>17.54</td>
</tr>
</tbody>
</table>

Answers: 50.97, 44.65, and 6.32 kJ/mol