The Vapor Pressure of Acetone at Low Temperatures

THESIS.

William Ure.
THE VAPOR PRESSURE

OF

ACETONE AT LOW TEMPERATURES.

by

William Ure

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THE VAPOR PRESSURE
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I. Introduction.

No measurements of the vapor pressure of acetone below 20°C are available up to the present time with the exception of two isolated figures at -59° and -78° by O. Stern, published in the Tables de Constantes. Above 20° the vapor-pressure has been measured by Regnault, and Ramsay and Young. In conjunction with measurements which have just been made on the density and viscosity of acetone at low temperatures, it was thought that it would be of value to obtain the vapor-pressure curve of acetone from -20°C down to the freezing point -94.6°C.

II. Experimental

(a) Method.

The static method was used, with a differential tensimeter in which the difference in pressure in vacuo between that of acetone and a standard liquid was measured by the difference of level of mercury in a manometer. It was intended at first to use ethyl alcohol as a standard of vapor pressure, dehydrating it by means of lime, but it was difficult to get out the

3 Phil. Trans. 178 A 313, 1887.
last trace of water, and to prevent the alcohol absorbing water while being handled, hence, this was given up, and benzene was used instead. Some very pure benzene was available and this would not absorb water so readily.

Mercury was used as a gauge liquid, although it was originally intended to use a liquid of lower specific gravity for greater accuracy. It was difficult, however, to find a liquid of the desired specific gravity, such that the apparatus would not be unwieldy and at the same time a liquid which would not dissolve or act upon either the acetone or the benzene.

(b) Purification of Materials.

1. Acetone - The acetone was purified by crystallization with sodium iodide after the method of Shipsey¹ and Werner, as follows:

500 cc. of C.P. acetone were distilled once with a still head. 100 gms. of anhydrous sodium iodide were dissolved in the fresh distillate by heating gently on a water bath. The solution was then cooled to about -20° in ethyl acetate and carbon dioxide snow. The crystals of the compound NaIoc\(\text{CH}_3\) which separated out were drained off so far as possible from the mother liquor, quickly transferred to a dry flask attached

¹ J.Chem.Soc. 103-1255, 1913
to a condenser and receiver, and the acetone rapidly distilled off by gentle heating. The mother liquor was treated with a further quantity of NaI and the process repeated until about 250 cc. of distilled acetone were obtained. This quantity was dried with calcium chloride for a day or so and then distilled. The product had a specific gravity at 20°, as measured by pyknometer, of 0.79170, and a refractive index of 1.3597. (D line) Landolt\(^1\) gives for \(D_{aq} = 0.7917\) and Korten\(^2\) \(n_D = 1.3593\) so that the acetone obtained was very pure.

2. Benzene.

500 cc. of C.P. benzene were treated with 25 cc. concentrated \(\text{H}_2\text{SO}_4\) and the mixture shaken up three times a day, the acid being changed every two days. The benzene was treated with three separate portions of concentrated \(\text{H}_2\text{SO}_4\). After this treatment the benzene gave no violet coloration (for thiophene) with isatin. The benzene was then separated from the acid and treated with 200 cc. of distilled water. The mixture was neutralized with sodium carbonate, and the benzene washed three times with distilled water. It was then separated from the water and refluxed over sodium for about 4 hours. The benzene was then distilled twice. The product had a specific gravity of 0.87900 at 20° (pyknometer). Young\(^3\) gives \(D_{aq} = 0.8790\).

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1 Pogg. 122. 545.
2 Diss. Bonn. 1890.

Mercury was used which had previously been distilled twice. It was further distilled in vacuo with a small amount of air bubbling through it to oxidize any base metals, after the method suggested by Hulett.¹

(c) Thermometer.

The temperatures were measured with a platinum resistance thermometer of the bridge type, Leeds & Northrup Meter Bridge No. 4201 being used, reading to .0001 ohm, corresponding to about .01° C. The resistance element was contained in a quartz tube which also contained gold compensating leads. The galvanometer was set on a solid pillar and observed with a lamp and scale. The resistance of the leads was eliminated by taking the mean of two readings at opposite positions of a commutator switch.

The thermometer was standardized by the Bureau of Standards in September, 1923, and its in the Callendar equation found to be 1.50. On installation the thermometer was checked at 0° C and observations made at the temperatures of ether and solid carbon dioxide (-78.34° C at atmospheric pressure) and boiling oxygen (-182.95° C), to determine the deviations from the parabolic formula. At -78.34° the thermometer read .04° low, and at -182.95°, 1.77° low. These values correspond

to Hennings\textsuperscript{1} corrections to the parabolic formula, and these corrections were accordingly used. A chart of resistance against temperature was plotted and used to estimate the temperatures at which the vapor pressure measurements were made.

(d) Apparatus and Measurements.

Fig. 1 shows the tensimeter which was made of soft glass. The bulbs were filled with acetone and benzene and were directly connected to the manometer arms. Great difficulty was experienced in getting all of the air out of the apparatus, and the following procedure was finally adopted. The manometer was filled with the required amount of mercury and the whole apparatus evacuated through tubes $cc$, the bulbs $bb$ being closed without filling with liquid. At the same time the mercury was heated to boiling to drive out enclosed air. For evacuation the tubes $cc$ were connected through a $T$ tube to an oil pump. Between this and the apparatus, was connected a trap immersed in liquid air for the purpose of retaining any volatile ingredients of the oil and of preventing the vapors from the apparatus from impairing the efficiency of the pump. Medium oil of the best grade was used, and was previously heated to $150^\circ$. At first a pressure gauge was connected in the system but it was found that the pump would reduce the pressure to less than one millimeter, so this was left out to minimize the danger

\textsuperscript{1} Ann. der Physik, 40, 1913.
leaks. With this type of apparatus it is not necessary to reduce to a high degree of vacuum since the residual pressure is equalized on both sides of the manometer. Less than one millimeter pressure is therefore sufficient.

After the mercury has reached boiling, the apparatus was allowed to cool and then air readmitted through cc. The bulbs were then opened at x, x filled with the liquids and sealed off. The bulbs were then immersed in liquid air and the apparatus evacuated as before for half an hour with the benzene and the acetone both solid and exerting very low vapor-presures. The mercury was heated again to some extent. The apparatus was then sealed off from the pump at cc. To test for the presence of air the tensimeter was set up and measurements made of vapor pressure at 20°, the attempt being made to check with Regnault's result of 179.63 mm. After this first evacuation the measurement obtained was 5 cm. too high. This was believed to be due to the solution of a certain amount of air in the acetone at atmospheric pressure. This would be retained on freezing in spite of the lowered pressure and would be liberated on warming up in vacuo. This view was upheld by the fact that on immersion of the bulbs in liquid air there was still a difference in level of mercury of about 4 cm. The apparatus was therefore opened at cc and re-evacuated, then sealed off. The vapor-pressure as measured at 20° was still a little higher than Regnault's
result, but it was believed that this was not air, and a series of measurements was made.

In making measurements the apparatus was set up as shown in Plate I. The manometer was immersed in the glass-sided thermostat, the temperature of which was kept at 25° to within 1/5° by means of a heating bulb B and a toluene regulator H operating an electro-magnetic relay. The thermostat was stirred by the zig-zag stirrer K, run by the motor M. The benzene bulb was immersed in a Dewar flask A, and was kept at 0° in ice and distilled water. The temperature of this bath could be kept constant to within 1°. It was stirred by the glass propeller P.

The acetone bulb was contained in the large Dewar flask D which was about 10 cm. diameter by 30 cm. long inside dimensions. This was the low temperature bath, and at temperatures below zero, ethyl ether was used as a medium and was stirred by the double propeller P. Above zero, water was used in this bath and the temperature regulated by means of hot water or ice to within 0.02°. For measurements from 0° to -75° solid carbon dioxide was used to lower and regulate the temperature. This was added by hand, and in addition a tube T immersed in the bath was partly filled with the snow. This served to hold the temperature down, although the actual regulation was done by the addition of small amounts of carbon dioxide at intervals.

Below -75°, liquid air was used as a cooling agent. This was contained in a small Dewar flask as shown in fig. 2 and was
used after the manner devised by Henning. Liquid air was forced directly into the ether in flask D by the hydrostatic head in the cylinder d. The depth of immersion of the tube t could be varied and hence the quantity of liquid air forced into the bath varied until it just compensated for the heat absorbed by the bath.

Below 0° the temperature could be kept constant to within .2° and the readings in all cases were taken at zero deflection of the galvanometer, indicating that the bath was exactly at the desired temperature. The thermometer is shown at t.

Readings were made by means of a cathetometer set at four feet from the apparatus, equipped with a metal scale and vernier reading to .005 cm. Readings were taken approximately every five degrees from +20° to -105°. In most cases it was possible to get consistent results to within .005 cm.

The benzene at 0° was kept in the meta table liquid form, and Young's value for the vapor-pressure at this temperature was accepted.

\[(p = 26.54 \text{ mm.})\]

In order to corroborate the values thus obtained a direct reading apparatus was constructed, and is shown in fig. 3. This consisted of an acetone bulb directly connected to a small manometer m. The manometer was first constructed and

1 Ztschr. Instrumentkunde 33. 1913. 33.
filled and then attached to the bulb which was filled. The apparatus was evacuated through o with the bulb immersed in ethyl acetate and carbon dioxide at about -78°, the small amount of vapor present at that temperature serving to sweep out any residual air. It was then sealed off at 0. A series of readings were taken, then the apparatus was opened and re-evacuated, after which the results were found to agree with those taken after the first evacuation. The results obtained with this type of apparatus agreed very closely with those obtained with the other from +20° to -25° as shown in Table I. Owing to the difficulty of making an accurate manometer, the latter results are taken as more reliable.

III. Results.

The vapor pressures of acetone from +20° C to -105° are shown in Table I. I. Pressures are expressed in millimeters of mercury at 0° C, to obtain which, the observed height of mercury at 25° was multiplied by \( \frac{13.5340}{13.5955} \) which is the ratio of the densities of mercury at 25° and 0°. The values are given to two places of decimals. They are reliable to within .1 mm. and are probably correct to .05 mm. The temperatures are expressed in both Centigrade and absolute degrees, and are given to hundredths of a degree since at the higher temperatures .01° corresponds to a change in pressure of over .05 mm.
### Table I.

<table>
<thead>
<tr>
<th>Centigrade</th>
<th>Absolute Temp.</th>
<th>Vapor - Pressure mm. Hg. at 0°C.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temp.</td>
<td>I</td>
</tr>
<tr>
<td>19.89</td>
<td>292.89°</td>
<td>185.57</td>
</tr>
<tr>
<td>14.87</td>
<td>287.87</td>
<td>150.00</td>
</tr>
<tr>
<td>9.87</td>
<td>282.87</td>
<td>119.42</td>
</tr>
<tr>
<td>4.82</td>
<td>277.82</td>
<td>94.09</td>
</tr>
<tr>
<td>0</td>
<td>273.00</td>
<td>75.25</td>
</tr>
<tr>
<td>-5.15</td>
<td>267.35</td>
<td>57.90</td>
</tr>
<tr>
<td>-10.15</td>
<td>262.85</td>
<td>44.96</td>
</tr>
<tr>
<td>-15.15</td>
<td>257.85</td>
<td>34.80</td>
</tr>
<tr>
<td>-20.21</td>
<td>252.79</td>
<td>26.79</td>
</tr>
<tr>
<td>-25.07</td>
<td>247.93</td>
<td>20.91</td>
</tr>
<tr>
<td>-30.07</td>
<td>242.93</td>
<td>16.13</td>
</tr>
<tr>
<td>-34.96</td>
<td>238.04</td>
<td>12.35</td>
</tr>
<tr>
<td>-39.89</td>
<td>233.11</td>
<td>9.86</td>
</tr>
<tr>
<td>-44.81</td>
<td>228.19</td>
<td>7.77</td>
</tr>
<tr>
<td>-49.62</td>
<td>223.38</td>
<td>6.53</td>
</tr>
<tr>
<td>-54.53</td>
<td>218.47</td>
<td>5.15</td>
</tr>
<tr>
<td>-59.47</td>
<td>213.53</td>
<td>4.29</td>
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<tr>
<td>-64.57</td>
<td>208.43</td>
<td>3.59</td>
</tr>
<tr>
<td>-69.44</td>
<td>203.56</td>
<td>3.09</td>
</tr>
<tr>
<td>-74.41</td>
<td>198.59</td>
<td>2.59</td>
</tr>
<tr>
<td>-79.40</td>
<td>193.60</td>
<td>2.20</td>
</tr>
<tr>
<td>-84.35</td>
<td>188.65</td>
<td>1.95</td>
</tr>
<tr>
<td>-89.52</td>
<td>183.48</td>
<td>1.65</td>
</tr>
<tr>
<td>-94.35</td>
<td>178.65</td>
<td>1.40</td>
</tr>
<tr>
<td>-99.84</td>
<td>173.16</td>
<td>1.15</td>
</tr>
<tr>
<td>-104.75</td>
<td>168.25</td>
<td>0.85</td>
</tr>
</tbody>
</table>

Column II shows the measurements made with the direct apparatus at temperatures ± 20° to -25°. The agreement on the whole is very good, and justifies the acceptance of the results obtained with the tensimeter.

Fig. 4 shows the vapor-pressure curve of acetone, obtained by plotting the observed vapor-pressures against temperature. A very smooth curve is obtained from the experimental points. It is to be noticed that the point at -99.84° falls on the
Fig. 4.
Vapor-Pressure Curve of Acetone

P in mm of mercury at 0°C.
continuation of the smooth curve past the freezing point -94.6 indicating that the acetone was a super-cooled liquid at that temperature. At -104.75 the acetone was seen to be solid, and this point falls away from the curve as would be expected.

The differential equation of this curve is the Clausius-Clapeyron equation

\[
\frac{d\ln p}{dT} = \frac{\Delta H_v}{RT^2}
\]

where \( \Delta H_v \) is the latent heat of vaporization and varies with the temperature.

Table II shows the results obtained by other investigators within this temperature range, compared with those obtained in this research. The latter values are obtained from the curve. The results do not agree, and it is to be noticed that the value obtained at 20° in this work lies between those of the other investigators.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Regnault</th>
<th>Ramsay &amp; Young</th>
<th>Stern</th>
<th>Ure</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>179.63</td>
<td>197.9</td>
<td>1.3</td>
<td>4.3</td>
</tr>
<tr>
<td>-59</td>
<td></td>
<td></td>
<td>0.5</td>
<td>2.3</td>
</tr>
<tr>
<td>-78</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

IV. Latent Heat of Vaporization.

The latent heat of vaporization of acetone may be calculated from the data obtained and the Clausius-Clapeyron equation

\[
\frac{d\ln p}{dT} = \frac{\Delta H_v}{RT^2}
\]

in which \( \ln p \) is the natural logarithm of the vapor-pressure, \( \Delta H_v \) the heat of vaporization in calories per gram-molecule,
T the absolute temperature and R the gas constant (1.985).

If Q is assumed constant over a certain range of temperature the above equation may be integrated to give

\[
Q = 4.571 \frac{T_2 T_1}{T_2 - T_1} \log_{10} \frac{P_2}{P_1}
\]

where \( P_1 T_1 \) and \( P_2 T_2 \) are corresponding quantities, and Q is the average latent heat over the interval from \( T_1 \) to \( T_2 \). In this way the average latent heat was calculated over the ranges of temperature +20° to -20°C, -20° to -60°, and -60° to -90°.

Table III shows these values expressed in calories per gram of liquid. It is to be noticed that the latent heat of vaporization of acetone decreases as the temperature is lowered, which is the opposite to that of water and most liquids. This was noticed by Regnault\(^1\) at temperatures above zero. At 0° he found the value to be 139.90 cal., at +80°, 166.51 cal. and at 140°, 181.69 cal.

<table>
<thead>
<tr>
<th>Table III.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp. range</td>
</tr>
<tr>
<td>+20°C to -20</td>
</tr>
<tr>
<td>-20 to -60</td>
</tr>
<tr>
<td>-60 to -90</td>
</tr>
</tbody>
</table>

V. Summary

1. Pure acetone has been prepared by crystallization with

\(^1\) Ann.Chim.Phys. (3) 26, 278 - 1849
sodium iodide after the method of Shipsey and Werner.

2. The differential tensimetric method has been successfully applied to measuring the vapor-pressure of a pure liquid.

3. The vapor-pressure of acetone has been measured from +20°C to -105°C.

4. The latent heat of vaporization of acetone has been calculated from the observed vapor-pressures over different temperature ranges from +20°C to -90°C.

In conclusion I wish to express my thanks to Dr. E.H. Archibald for his never-failing advice and assistance, and to the Research Council of Canada for its financial assistance in carrying on this work.

Department of Chemistry.
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