CRYOSCOPIC CONSTANT, HEAT OF FUSION, AND HEAT CAPACITY OF CAMPHOR

By Mikkel Frandsen

ABSTRACT

In order to determine the cryoscopic constant of camphor the latent heat of fusion of this substance was measured calorimetrically. Values for the heat capacities of solid and liquid camphor were obtained at the same time. The determinations were made on synthetic camphor, the freezing point of which was found to be 178.43° C. Two samples of this material and one of pure silver, serving as a reference substance, were sealed in evacuated, thin-walled glass tubes, and successively heated to constant, well-defined temperatures in a narrow glass tube surrounded by the vapors of various liquids, boiling in the range from 20° to 212° C. In each case the heat content of the sample was measured by transferring it to a silvered Dewar tube, containing about 300 g of water. From a plot of the heat content against the temperature the following results were obtained:

The latent heat of fusion at 178.4° C, \( l_f = 10.74 \pm 0.40 \) cal, or, \( L_f = 1,630 \pm 60 \), cal mole\(^{-1}\). The cryoscopic constant, \( k_f = 37.7 \pm 1.4 \) C. mole\(^{-1}\) kg. The heat capacity of crystalline camphor in the range from 20 to 178.4° C, \( c_{(\text{solid})} = (0.4208 \pm 0.000265) t + 0.0035 \), cal g\(^{-1}\) C.\(^{-1}\), or, \( C_{(\text{solid})} = (64.0 \pm 0.033) t + 0.5 \), cal mole\(^{-1}\) C.\(^{-1}\). The heat capacity of liquid camphor in the range from 178.4° to 210° C, \( c_{(\text{liquid})} = 0.571 \pm 0.045 \), cal g\(^{-1}\) C.\(^{-1}\), or, \( C_{(\text{liquid})} = 87 \pm 7 \) cal mole\(^{-1}\) C.\(^{-1}\).

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I. INTRODUCTION

Camphor is often used as a solvent in determinations of molecular weights by the freezing-point method. Unfortunately, however, there seems to be some difference of opinion in regard to the value of the cryoscopic constant for this substance. From a large number of determinations Jouiaux\(^1\) has obtained the average value 49.5, and Efremov's\(^2\) determinations lead to an average of 48.7. Rast,\(^3\) on the other hand, gives the value as 39.7, which also was used by Smith and Young,\(^4\) while Houben\(^5\) and Carlsohn\(^6\) used the value 40.0.

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\(^1\) Jouiaux, Compt. rend., 154, p. 1592; 1912.
\(^2\) Efremov, Tables Annuelles Internationales de Constants et Données Numériques, 5, p. 853; 1922.
\(^3\) Rast, Ber., 55, pp. 1061, 3727; 1922.
\(^4\) Smith and Young, J. Biol. Chem., 75, p. 239; 1927.
\(^5\) Houben, J. prakt. Chem., 105, p. 27; 1922.
\(^6\) Carlsohn, Ber., 66, p. 473; 1927.

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Since the true cryoscopic constant of a substance is completely defined by its melting point and latent heat of fusion, a determination of these two properties should lead to a clarification of the situation with respect to this constant for camphor. The equipment required for these measurements being at hand in connection with another investigation, advantage was taken of the possession of a small sample of pure synthetic camphor to carry out a few determinations. Incidentally, approximate values for the heat capacities of solid and liquid camphor, respectively, were also obtained.

Figure 1.—Cooling curve of camphor

II. MATERIAL

The material on which the determinations were made was synthetic camphor, which had been purified by several recrystallizations from ethyl alcohol. The freezing point of this material was determined in a small silvered Dewar tube, using the procedure described by Washburn. A cooling curve obtained as an average of four single curves is shown in Figure 1. From this curve the freezing point is found to be

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This material was supplied by Dr. C. L. Reese, of the DuPont Co.
Cryoscopic Constant of Camphor

178.43 ± 0.04°C. A comparison with the determinations made by Komppa, Haller, and Johnston, namely, 178° to 178.5°C. and 178.8°C., respectively, leads to the conclusion that the material was sufficiently pure. It may not have been absolutely pure, however, since an equilibrium cooling curve should have the shape indicated by the dotted lines in Figure 1. Possibly complete equilibrium was not attained toward the end of the crystallization owing to the thermometer becoming covered with solid camphor.

III. CALORIMETRIC APPARATUS AND PROCEDURE

In this investigation the calorimetric method of mixtures was employed in a manner substantially that described by Andrews, Lynn, and Johnston.

The calorimeter consisted of a silvered Dewar tube, 5.1 × 25.4 cm, surrounded by appropriate insulating material, and charged with about 300 grams of water. The heat capacity of the calorimeter was accurately determined by electrical calibration and the procedure was standardized against metallic silver as in the experiments of Andrews, Lynn, and Johnston.

The true temperature rise in the calorimeter was found by the graphic method described by Dickinson.

On account of the low thermal conductivity of solid camphor it was found necessary, first, to leave the samples in the high-temperature bath for at least four hours; second, to use an after-period of 30 minutes; and third, to remove the sample of camphor from the calorimeter before observing the final rate of temperature change.

Corrections were applied for the heat given up to the calorimeter by the suspending wire and glass containing-tube, and for the vaporization of a small amount of camphor at the higher temperatures.

Corrected quantity of heat given up by the sample, divided by the mass of camphor, is the quantity of heat required to raise the temperature of 1 g of camphor from the final temperature of the calorimeter to the initial temperature of the sample. This is equal, within the limit of experimental error, to the heat content of 1 g of camphor at its initial temperature and under any constant low pressure, if the heat content at the final temperature of the calorimeter is taken as zero. The final temperature of the calorimeter was not the same in all experiments, although it was always close to 20°C. To make the results comparable, the values of heat content were all reduced to the basis of heat content = 0 at 20°C., using the value 0.425 calories per gram for the heat capacity of camphor at room temperature, a value which results from this investigation.

Komppa, Ber., 41, p. 4473; 1908.
Haller, Compt. rend., 106, p. 68; 1887.
Dickinson, B. S. Bull., 11, p. 234; 1915.
IV. EXPERIMENTAL RESULTS

1. DATA AND DISCUSSION

The experimental results are shown in Table 1. The heat contents in Table 1 have been plotted against the temperature as shown in Figure 2. From this figure it is seen that the duplicate determinations on solidified camphor are in good agreement. The fact that the curve for this material when extrapolated passes through the point (0, 20) indicates that the results are not vitiated by the most probable types of systematic errors.
Cryoscopic Constant of Camphor

Table 1.—Heat content of synthetic camphor at various temperatures

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Vapor bath</th>
<th>Temperature</th>
<th>$H_r-H_s$</th>
<th>State of camphor</th>
<th>Run No.</th>
<th>Vapor bath</th>
<th>Temperature</th>
<th>$H_r-H_s$</th>
<th>State of camphor</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ethyl ether</td>
<td>33.8</td>
<td>5.83</td>
<td></td>
<td>11</td>
<td>Aniline</td>
<td>182.5</td>
<td>82.97</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>34.1</td>
<td>5.71</td>
<td></td>
<td>12</td>
<td></td>
<td>182.7</td>
<td>83.44</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Methyl alcohol</td>
<td>64.4</td>
<td>19.31</td>
<td></td>
<td>13</td>
<td>Dimethyl-aniline</td>
<td>192.6</td>
<td>89.42</td>
<td>Lq-100.1</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>64.5</td>
<td>18.64</td>
<td></td>
<td>14</td>
<td></td>
<td>193.9</td>
<td>88.98</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Water</td>
<td>100.1</td>
<td>54.87</td>
<td>Solidified melt.</td>
<td>15</td>
<td>Nitro-benzene</td>
<td>210.1</td>
<td>100.1</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>100.1</td>
<td>34.59</td>
<td></td>
<td>16</td>
<td></td>
<td>210.3</td>
<td>97.56</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Chlоро-benzene</td>
<td>130.6</td>
<td>48.50</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>130.1</td>
<td>48.30</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Butyl butyrate</td>
<td>163.6</td>
<td>63.61</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>164.1</td>
<td>63.30</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The duplicate determinations on liquid camphor at $193^\circ$ and $210^\circ$ C. do not agree so well, probably on account of incipient decomposition of the camphor caused by prolonged heating at those temperatures.

For two reasons it is important to find out whether complete crystallization of the fused camphor took place when the sample was plunged into water at room temperature. If so (1) the slope of the curve for solidified camphor represents the heat capacity of solid, crystalline camphor; and (2) the difference in the ordinates of the two heat content curves at the melting point represents the latent heat of fusion of the same substance. A crystallographic examination of a sample of camphor which had been quenched from the liquid state on a microscope slide showed no detectable amount of vitreous material. Crystallization in the calorimeter may, therefore, be assumed to have been complete.

2. LATENT HEAT OF FUSION

From Figure 2 the latent heat of fusion, determined as the difference in heat content of liquid and crystalline camphor at the freezing point, is found to be

$$l_r = 10.74 \pm 0.40, \text{ cal.}_{15} \text{ per gram}$$

or

$$L_r = 1630 \pm 60, \text{ cal.}_{15} \text{ per mole}$$

at $178.4^\circ$ C.\(^1\)

3. THE CRYOSCOPIC CONSTANT

The cryoscopic constant, $k_r$, of a substance is defined as the limiting value for infinite dilution of the freezing point lowering, $\Delta t_r$, produced per mole of solute in 1,000 g of the substance, or

$$k_r = \lim_{N_1 \to 0} \left( \frac{\Delta t_r}{N_1} \right)$$

where $N_1$ is the concentration of the solute in moles per 1,000 g of solvent. The cryoscopic constant may be calculated from the formula

$$k_r = 1.987 \frac{T_r^2}{1,000 l_r} \text{ C. mole}^{-1} \text{ kg}$$

\(^1\) Attempts to calculate the heat of fusion, by means of the Thomson-Kirchhoff relation, from the vapor pressure curves of the two phases in the neighborhood of the freezing point were unsuccessful, owing to lack of accuracy in the available data, the two curves apparently intersecting at $160^\circ$ instead of $178^\circ$ C.

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in which \( T_r \) is the melting point of the solvent in \(^oK\) and \( l_r \) its latent heat of fusion in cal.\(_{15}\) per gram. Substituting the values for camphor

\[
T_r = 178.4 + 273.1
\]

and

\[
l_r = 10.74 \pm 0.40
\]

gives

\[
k_r = 37.7 \pm 1.4, \text{ } ^o\text{C. mole}^{-1}\text{kg}
\]

for the cryoscopic constant of camphor.

4. HEAT CAPACITIES

For the curve in Figure 2 showing the heat content of solidified camphor, the following equation has been derived:

\[
H_t = (-8.459 + 0.4208 t + 0.0001076 t^2) \pm 0.25, \text{ cal.}_{15}\text{g}^{-1}
\]

By differentiation of this equation the heat capacity of solid camphor is found to be

\[
c_{\text{solid}} = \frac{dH_t}{dt} = (0.4208 + 0.000215 t) \pm 0.0035, \text{ cal.}_{15}\text{g}^{-10}\text{C.}^{-1}
\]

or

\[
C_{\text{solid}} = (64.0 + 0.033 t) \pm 0.5, \text{ cal.}_{15}\text{mole}^{-10}\text{C.}^{-1}
\]

These three equations apply to solid camphor, in the range from \(20^o\) to \(178.4^o\) C.

Similarly the slope of the upper curve in Figure 2 gives for the heat capacity of liquid camphor

\[
c_{\text{liquid}} = 0.571 \pm 0.045, \text{ cal.}_{15}\text{g}^{-10}\text{C.}^{-1}
\]

or

\[
C_{\text{liquid}} = 87 \pm 7, \text{ cal.}_{15}\text{mole}^{-10}\text{C.}^{-1}
\]

in the range from \(178.4\) to \(210^o\) C.

Strictly speaking, these heat capacities are the heat capacities of the solid and liquid camphor, respectively, under an external pressure at all times equal to the vapor pressure. They do not differ appreciably, however, from the heat capacities at a constant pressure of 1 atmosphere.

V. CONCLUSIONS

From calorimetric measurements the following thermal data for pure synthetic camphor were obtained:

The latent heat of fusion at \(178.4^o\) C.

\[
l_r = 10.74 \pm 0.40, \text{ cal.}_{15}\text{g}^{-1}
\]

or

\[
L_r = 1630 \pm 60, \text{ cal.}_{15}\text{mole}^{-1}
\]

The cryoscopic constant,

\[
k_r = 37.7 \pm 1.4^o\text{C. mole}^{-1}\text{kg}
\]
The heat capacity of solid, crystalline camphor

\[
c_{\text{solid}} = (0.4208 + 0.000215 t) \pm 0.0035, \text{ cal.} \text{g}^{-10} \text{C.}^{-1}
\]

or

\[
C_{\text{solid}} = (64.0 + 0.033 t) \pm 0.5, \text{ cal.} \text{mole}^{-10} \text{C.}^{-1}
\]
in the range from 20° to 178.4° C.

Similarly, for liquid camphor,

\[
c_{\text{liquid}} = 0.571 \pm 0.045, \text{ cal.} \text{g}^{-10} \text{C.}^{-1}
\]

or

\[
C_{\text{liquid}} = 87 \pm 7, \text{ cal.} \text{mole}^{-10} \text{C.}^{-1}
\]
in the range from 178.4° to 210° C.

The freezing point, obtained from the cooling curve, was found to be 178.43° ± 0.04° C.

VI. ACKNOWLEDGMENT

The author is greatly indebted to E. W. Washburn, of this bureau, under whose direction this work was done.

WASHINGTON, June 2, 1931.