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Leon J. Shereshefsky

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THE CORRESPONDING STATE OF MAXIMUM SURFACE TENSION OF SATURATED VAPORS

BY J. L. SHERESHEFSKY*

Making use of the expression developed by Laplace for the cohesion pressure of a liquid, and resorting to the well known phenomenon of capillary rise, N. Barbulescu1 has recently derived for the surface tension of a saturated vapor the equation

\[ \sigma_v = \frac{rh}{2} \rho_v \]

(1)

where \( \sigma_v \) is the surface tension of the vapor, \( h \) the height of rise of the liquid in a capillary of radius \( r \), and \( \rho_v \) the density of the saturated vapor.

By means of this equation the values of \( \sigma_v \) for several saturated vapors at various temperatures were calculated and found to pass a maximum in the neighborhood of the critical temperature, the ratio of the temperature at the maximum to the critical temperature being approximately constant.

As this behavior of vapors seems to be general and the maximum apparently characteristic of all substances, it was considered of interest to relate it to the critical constants, and if possible to deduce an expression that would define this maximum.

The surface tension of a liquid at any temperature is given by

\[ \sigma_l = \frac{rh}{2} (\rho_l - \rho_v) \]

(2)

where \( \sigma_l \) is the surface tension of the liquid, \( h \) the height of rise of the liquid in a capillary of radius \( r \), and \( \rho_l \) the density of the liquid. Combining equations (1) and (2) the following relation for the surface tension of a vapor in equilibrium with its liquid is obtained:

\[ \sigma_v = \sigma_l \left( \frac{\rho_v}{\rho_l - \rho_v} \right) \]

(3)

To express \( \sigma_v \) as a function of temperature equation (3) may be combined, either with the theoretical equations of van der Waals2

\[ \sigma_l = a (1 - T/T_c)^{3/2} \]

(4)

and

\[ -V_v - V_l = b (1 - T/T_c)^{1/2} \]

(5)

or with the empirical equation of D. B. Macleod3

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* Industrial Fellow, Mellon Institute of Industrial Research.
1 Physik. Z., 31, 48 (1930).
3 Trans. Faraday, 18, 38 (1923).
\[ \sigma_1 = c (\rho_1 - \rho_v)^4 \]  
\[ (6) \]

and the one by D. H. Goldhammer

\[ \rho_1 - \rho_v = k (1 - T/T_c)^{1/3} \]  
\[ (7) \]

In these equations \(a, b, c, k\) are constants characteristic of the compound, \(V\), and \(V_v\) the specific volume in the vapor and liquid states respectively, and \(T\) is the absolute temperature. The van der Waals equations hold only for a very limited range of temperatures near the critical, while equations \((6)\) and \((7)\) are remarkably accurate for a wide range of temperatures up to \(0.98T_c\). In using the latter the lack of a theoretical foundation is compensated by the extreme accuracy of the results.

Combining equation \((3)\) with \((6)\) and \((7)\) we obtain

\[ \sigma_v = K(1 - T/T_c)\rho_v \]  
\[ (8) \]

an expression relating the surface tension of a saturated vapor with temperature. Differentiating, it gives

\[ \frac{d\sigma_v}{dT} = K \left[ (1 - \frac{T}{T_c}) \frac{d\rho_v}{dT} - \frac{\rho_v}{T_c} \right] \]

At the maximum point

\[ \left(1 - \frac{T}{T_c}\right) \frac{d\rho_v}{dT} - \frac{\rho_v}{T_c} = 0, \]

or

\[ \frac{d \ln \rho_v}{dT} = \frac{1}{T_c(1 - T/T_c)}, \]  
\[ (8a) \]

or

\[ \frac{d \log \rho_v}{dT} = \frac{0.4343}{T_c(1 - T_m/T_c)} \]  
\[ (9) \]

where \(T_m\) is the absolute temperature at which the saturated vapor has maximum surface tension.

By means of equation \((9)\) the values of \(T_m\) for nineteen different compounds were calculated, and are given in column IV of Table I. The values in column II were obtained graphically from data taken from the Inter. Crit. Tables, Vol. 5. A glance at column V will show that the ratio of the temperatures at which the maxima occur to the critical temperatures is constant, the mean value being \(0.910\) and the maximum deviations being less than \(\pm 1.5\) per cent. It is of interest to note that \(T_m/T_c\) for the polar compounds is somewhat higher than for the normal substances, indicating that even at these high temperatures there is a certain amount of molecular association.

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\(^1\) Z. physik. Chem., 71, 577 (1910).
MAXIMUM SURFACE TENSION OF SATURATED VAPORS

Table I

The Corresponding State of Maximum Surface Tension of Saturated Vapors

<table>
<thead>
<tr>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
<th>VI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substance</td>
<td>d log $\rho_v$</td>
<td>$T_e$</td>
<td>$T_m$</td>
<td>$\frac{T_m}{T_e}$</td>
<td>Percent Deviation from the Mean</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>.0093</td>
<td>479.3</td>
<td>423.7</td>
<td>.901</td>
<td>-0.99</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>.0093</td>
<td>507.9</td>
<td>461.2</td>
<td>.908</td>
<td>-0.22</td>
</tr>
<tr>
<td>n-Octane</td>
<td>.0087</td>
<td>569.3</td>
<td>519.2</td>
<td>.912</td>
<td>+0.22</td>
</tr>
<tr>
<td>Cyclo-hexane</td>
<td>.0076</td>
<td>554.1</td>
<td>497.0</td>
<td>.897</td>
<td>-1.43</td>
</tr>
<tr>
<td>Carbon Tetrachl.</td>
<td>.0077</td>
<td>556.1</td>
<td>499.7</td>
<td>.899</td>
<td>-1.21</td>
</tr>
<tr>
<td>Benzene</td>
<td>.0078</td>
<td>561.6</td>
<td>505.9</td>
<td>.901</td>
<td>-0.99</td>
</tr>
<tr>
<td>Fluorobenzene</td>
<td>.0078</td>
<td>559.6</td>
<td>504.2</td>
<td>.901</td>
<td>-0.99</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>.0076</td>
<td>633.1</td>
<td>576.0</td>
<td>.910</td>
<td>0.00</td>
</tr>
<tr>
<td>Bromobenzene</td>
<td>.0082</td>
<td>570.1</td>
<td>517.1</td>
<td>.907</td>
<td>-0.33</td>
</tr>
<tr>
<td>Methy Formate</td>
<td>.0097</td>
<td>487.1</td>
<td>442.3</td>
<td>.908</td>
<td>-0.22</td>
</tr>
<tr>
<td>Ethyl Acetate</td>
<td>.0098</td>
<td>524.1</td>
<td>479.8</td>
<td>.915</td>
<td>+0.55</td>
</tr>
<tr>
<td>Methyl Ether</td>
<td>.0106</td>
<td>400.0</td>
<td>359.2</td>
<td>.898</td>
<td>-1.32</td>
</tr>
<tr>
<td>Ethyl Ether</td>
<td>.0100</td>
<td>467.6</td>
<td>424.2</td>
<td>.907</td>
<td>-0.33</td>
</tr>
<tr>
<td>Acetone</td>
<td>.0100</td>
<td>508.1</td>
<td>464.9</td>
<td>.915</td>
<td>+0.55</td>
</tr>
<tr>
<td>Methyl Alcohol</td>
<td>.0109</td>
<td>513.1</td>
<td>473.3</td>
<td>.921</td>
<td>+1.21</td>
</tr>
<tr>
<td>Ethyl Alcohol</td>
<td>.0109</td>
<td>516.1</td>
<td>476.3</td>
<td>.922</td>
<td>+1.32</td>
</tr>
<tr>
<td>n-Propyl Alcohol</td>
<td>.0102</td>
<td>536.8</td>
<td>494.4</td>
<td>.921</td>
<td>+1.21</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>.0081</td>
<td>594.1</td>
<td>540.5</td>
<td>.911</td>
<td>+0.11</td>
</tr>
<tr>
<td>Propionic Acid</td>
<td>.0088</td>
<td>612.6</td>
<td>558.1</td>
<td>.920</td>
<td>+1.10</td>
</tr>
</tbody>
</table>

Mean .910

It is also of interest to show, since $T_m/T_e$ is a constant, that $\frac{d \ln \rho_v}{d \ln T}$ is a universal constant and equals 10.1.

Multiplying equation (8a) by $T_m$ we obtain

$$\frac{T_m d \ln \rho_v}{dT} = \frac{T_m}{T_e (1 - T_m/T_e)}$$

or

$$\frac{d \ln \rho_v}{d \ln T} = \frac{T_m/T_e}{(1 - T_m/T_e)} = U = \frac{.91}{1 - .91} = 10.1$$

In conclusion, I wish to take the opportunity to express my appreciation of the instructive discussions with Dr. M. Muskat of the Gulf Research Laboratory.
Summary

1. An expression relating surface tension of saturated vapors with temperature is deduced.

2. It is shown that the ratio of the temperature at which the surface tension is a maximum to the critical temperature is constant, i.e.

\[ \frac{T_m}{T_c} = 0.910 \] for all substances.

3. It is also shown that the slope of \[ \log \rho_v - \log T \] curve at \( T_m \) is a universal constant, \( U = 10.1 \). Here \( \rho_v \) is the vapor density and \( T \) absolute temperature.

Mellon Institute of Industrial Research,
Gulf Production Fellowship, Pittsburgh, Pa.,
April 10, 1930.