Statistical Thermodynamical Calculation of the Surface Entropy of Liquids

by

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(Received Nov. 21, 1964)

Abstract

The excess molar surface entropies of each surface layers are calculated applying the modified significant structure theory of liquid. The calculated excess molar surface entropy for the first top surface layer is slightly greater than the entropy of surface formation of ideal molecules, the latter is equal to R ln 2. The excess entropy for the second surface layer is small and that for the third layer is negligible at low temperatures.

The surface tensions of argon, nitrogen, methane, benzene and halogens are calculated applying the modified significant structure theory of liquid.

Introduction

Many workers show that surface of liquid is not a mathematical plane but it consists of several molecular layers. Through these several molecular layers, the density of the liquid undergoes gradual changes before it changes abruptly to the vapor phase. This is shown theoretically by Hill and Chang et al.

This leads to the thought that the randomness of molecules changes accordingly in the surface region of a liquid.
Chang and co-workers\textsuperscript{7} have calculated surface tension of various liquids applying the significant structure theory of liquid which was proposed by H. Eyring et al. Recently, the surface tensions of carbon tetrachloride,\textsuperscript{9} water,\textsuperscript{9} ethylene chloride,\textsuperscript{10} fluorine\textsuperscript{11} and ammonia\textsuperscript{12} have been calculated using the modified significant structure theory of liquid proposed by Chang et al. In this paper, the authors calculate the excess molar surface entropy for various liquids and surface tensions of argon, nitrogen, benzene and halogen-applying the latter theory.

**Partition function**

According to the theory of modified significant liquid structure,\textsuperscript{13} liquid may possess both solid-like and gas-like degrees of freedom, but the former is not necessarily equal to that of solid itself. The fractions of the two degrees of freedom are represented as $V_s/V$ and $(V-V_s)/V$, respectively, where $V_s$ is the molar volume of solid-like molecules in liquid and $V$ is the molar volume of liquid itself. Thus, the partition function can be written as follows:

$$F = \left[ \frac{b_s}{(1-e^{-b_s/kT})} \right]^{V_s/V} \cdot \left[ \frac{b}{b_s} \right]^{(V-V_s)/V} N,$$

where $b_s$ and $b$ are respectively the interatomic vibrational and molecular rotational partition functions for the solid-like and gas-like molecules. $E$, ang.\textsuperscript{0} are respectively the ground state energy and Einstein characteristic temperature of the solid-like molecules. And $n_i$ and $c$ are respectively the number of vacancies available to one of the solid-like molecules and the energy required for a hole-molecule pair to exchange positions, which can be written as,

$$n_s = \frac{V-V_s}{V} \quad \text{and} \quad c = \frac{aE_sV_s}{\kappa(V-V_s)RT},$$

$n$ and $a$ being the proportionality constant and $T$ is equal to $\hbar/(2\pi mkT)^{1/2}$.

It is assumed that the partition function for the surface layers of a non-polar liquid can be approximated as to have the same form as for the bulk liquid, except the correction for the ground state energy of the solid-like molecules as proposed by Chang et al.\textsuperscript{7} It is assumed further that for a polar liquid or for a liquid asymmetric molecule, molecules on the top surface layer will orientate and changes in rotational degrees of freedom will take place. For example, solid-like molecules of benzene cannot rotate in bulk liquid, but molecules on the top surface layer can rotate about the axis as shown theoretically by Mørensen and Eyring.\textsuperscript{14}

Thus, the authors assume that the solid-like molecules such as benzene and ammonia,\textsuperscript{12} which cannot rotate in bulk liquid, can rotate freely about the figure axis only in the first top surface layer, and if the molecules, such as water\textsuperscript{6} and ammonia,\textsuperscript{12} have appreciable electric moments, they can have the molecular orientation. However, the molecules in the other surface layers are practically in a symmetrical field that they shall have the same degrees of freedom as for the bulk liquid.

**Calculation and results**

The excess molar surface entropy of $i$-th surface layer is given by $\delta S_i = S_i - S_0$, where $S_i$ is molar entropy of $i$-th surface layer and $S_0$ is molar entropy of bulk liquid which can be obtained from the partition functions of $i$-th surface layer and of bulk liquid, respectively, that is,

$$S_i = -(\delta A_i/kT)_{Vi} = kT \ln F_i + kT \left( \frac{\partial \ln F_i}{\partial T} \right)_{Vi},$$

and the molar entropy of surface formation is given by

$$\delta S = \frac{1}{2} \sum_{i=1}^{n_l} \frac{(S_i-S_0)}{Q_i} = \frac{\delta A}{Q_i},$$

where $Q_i$ is the molar area of the first top surface layer and $Q_i$ is for the $i$-th surface layer. Since the layer thicknesses are the same for all the surface layers, $Q_i$ is equal to $V_i/V_0$, where $V_i$ is the molar volume of the $i$-th layer.

Therefore

$$\delta S = \frac{1}{2} \sum_{i=1}^{n_l} \frac{(S_i-S_0)}{V_i/V_0}.$$

The calculated excess molar surface entropies for various substances are listed in the following tables.

**Excess molar surface entropy**

<table>
<thead>
<tr>
<th>Substance</th>
<th>$T_{K}$</th>
<th>$\delta S$ (e.u.)</th>
<th>$\delta S$ (e.u.)</th>
<th>$\delta S$ (e.u.)</th>
<th>$\delta S$ (e.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Argon</td>
<td>83.96</td>
<td>1.856</td>
<td>0.286</td>
<td>0.027</td>
<td>2.206</td>
</tr>
<tr>
<td></td>
<td>87.49</td>
<td>1.698</td>
<td>0.219</td>
<td>0.034</td>
<td>1.983</td>
</tr>
<tr>
<td></td>
<td>97.76</td>
<td>1.586</td>
<td>0.227</td>
<td>0.035</td>
<td>1.886</td>
</tr>
<tr>
<td>Methane</td>
<td>T°K</td>
<td>$\Delta S_{1}$ e. u.</td>
<td>$\Delta S_{2}$ e. u.</td>
<td>$\Delta S_{3}$ e. u.</td>
<td>$\Delta S_{4}$ e. u.</td>
</tr>
<tr>
<td>------------</td>
<td>------</td>
<td>----------------------</td>
<td>----------------------</td>
<td>----------------------</td>
<td>----------------------</td>
</tr>
<tr>
<td>90.65 (T₁)</td>
<td>1.527</td>
<td>0.142</td>
<td>0.000</td>
<td>1.680</td>
<td></td>
</tr>
<tr>
<td>99.67</td>
<td>1.461</td>
<td>0.131</td>
<td>0.000</td>
<td>1.535</td>
<td></td>
</tr>
<tr>
<td>111.67 (T₂)</td>
<td>1.359</td>
<td>0.126</td>
<td>0.013</td>
<td>1.502</td>
<td></td>
</tr>
<tr>
<td>123.15</td>
<td>1.302</td>
<td>0.136</td>
<td>0.012</td>
<td>1.466</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Nitrogen</th>
<th>T°K</th>
<th>$\Delta S_{1}$ e. u.</th>
<th>$\Delta S_{2}$ e. u.</th>
<th>$\Delta S_{3}$ e. u.</th>
<th>$\Delta S_{4}$ e. u.</th>
</tr>
</thead>
<tbody>
<tr>
<td>63.30 (T₁)</td>
<td>1.709</td>
<td>0.183</td>
<td>0.000</td>
<td>1.919</td>
<td></td>
</tr>
<tr>
<td>68.41</td>
<td>1.578</td>
<td>0.158</td>
<td>0.000</td>
<td>1.731</td>
<td></td>
</tr>
<tr>
<td>77.34 (T₂)</td>
<td>1.495</td>
<td>0.154</td>
<td>0.017</td>
<td>1.685</td>
<td></td>
</tr>
<tr>
<td>99.52</td>
<td>0.901</td>
<td>0.237</td>
<td>0.042</td>
<td>1.216</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Carbon tetrachloride</th>
<th>T°K</th>
<th>$\Delta S_{1}$ e. u.</th>
<th>$\Delta S_{2}$ e. u.</th>
<th>$\Delta S_{3}$ e. u.</th>
<th>$\Delta S_{4}$ e. u.</th>
</tr>
</thead>
<tbody>
<tr>
<td>273.15</td>
<td>2.107</td>
<td>0.186</td>
<td>0.017</td>
<td>2.296</td>
<td></td>
</tr>
<tr>
<td>293.15</td>
<td>2.189</td>
<td>0.189</td>
<td>0.016</td>
<td>2.408</td>
<td></td>
</tr>
<tr>
<td>323.15</td>
<td>2.214</td>
<td>0.206</td>
<td>0.015</td>
<td>2.567</td>
<td></td>
</tr>
<tr>
<td>349.90 (T₂)</td>
<td>2.286</td>
<td>0.284</td>
<td>0.028</td>
<td>2.742</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Benzene</th>
<th>T°K</th>
<th>$\Delta S_{1}$ e. u.</th>
<th>$\Delta S_{2}$ e. u.</th>
<th>$\Delta S_{3}$ e. u.</th>
<th>$\Delta S_{4}$ e. u.</th>
</tr>
</thead>
<tbody>
<tr>
<td>278.68 (T₁)</td>
<td>2.408</td>
<td>0.179</td>
<td>0.011</td>
<td>2.613</td>
<td></td>
</tr>
<tr>
<td>288.15</td>
<td>2.283</td>
<td>0.170</td>
<td>0.014</td>
<td>2.483</td>
<td></td>
</tr>
<tr>
<td>328.15</td>
<td>2.204</td>
<td>0.206</td>
<td>0.018</td>
<td>2.451</td>
<td></td>
</tr>
<tr>
<td>353.35 (T₂)</td>
<td>2.147</td>
<td>0.238</td>
<td>0.032</td>
<td>2.448</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chlorine</th>
<th>T°K</th>
<th>$\Delta S_{1}$ e. u.</th>
<th>$\Delta S_{2}$ e. u.</th>
<th>$\Delta S_{3}$ e. u.</th>
<th>$\Delta S_{4}$ e. u.</th>
</tr>
</thead>
<tbody>
<tr>
<td>172.12 (T₁)</td>
<td>1.900</td>
<td>0.140</td>
<td>0.000</td>
<td>2.058</td>
<td></td>
</tr>
<tr>
<td>193.15</td>
<td>1.900</td>
<td>0.125</td>
<td>0.000</td>
<td>2.036</td>
<td></td>
</tr>
<tr>
<td>233.05 (T₂)</td>
<td>2.010</td>
<td>0.215</td>
<td>0.019</td>
<td>2.272</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bromine</th>
<th>T°K</th>
<th>$\Delta S_{1}$ e. u.</th>
<th>$\Delta S_{2}$ e. u.</th>
<th>$\Delta S_{3}$ e. u.</th>
<th>$\Delta S_{4}$ e. u.</th>
</tr>
</thead>
<tbody>
<tr>
<td>265.85 (T₁)</td>
<td>2.028</td>
<td>0.171</td>
<td>0.000</td>
<td>2.217</td>
<td></td>
</tr>
<tr>
<td>293.15</td>
<td>2.024</td>
<td>0.171</td>
<td>0.000</td>
<td>2.214</td>
<td></td>
</tr>
<tr>
<td>323.15</td>
<td>2.088</td>
<td>0.203</td>
<td>0.000</td>
<td>2.317</td>
<td></td>
</tr>
</tbody>
</table>

The surface tensions and their contributions to each surface layers of argon, nitrogen, methane, benzene and halogens calculated by the iteration method, proposed by Chang et al.  applying the modified significant structure theory of liquid and halogens are tabulated in the following tables. And also the surface tensions of carbon tetrachloride, fluorine, ethylenechloride, water, and ammonia can be found in the previous papers which were calculated by the similar method.

### Surface tension

#### Argon

<table>
<thead>
<tr>
<th>T°K</th>
<th>1st</th>
<th>2nd</th>
<th>3rd</th>
<th>calc. (dyne/cm)</th>
<th>obs. (dyne/cm)</th>
<th>Δ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>85.90 (T₁)</td>
<td>65.52</td>
<td>12.72</td>
<td>1.76</td>
<td>13.37</td>
<td>13.5</td>
<td>-0.96</td>
</tr>
<tr>
<td>87.49 (T₂)</td>
<td>84.76</td>
<td>13.36</td>
<td>1.67</td>
<td>12.48</td>
<td>12.5</td>
<td>-0.96</td>
</tr>
<tr>
<td>97.76</td>
<td>51.64</td>
<td>16.13</td>
<td>2.22</td>
<td>9.95</td>
<td>9.9</td>
<td>0.56</td>
</tr>
</tbody>
</table>
### Nitrogen

<table>
<thead>
<tr>
<th>$T^\circ K$</th>
<th>1st $%$</th>
<th>2nd $%$</th>
<th>3rd $%$</th>
<th>$\gamma_{calc.}$ (dyne/cm)</th>
<th>$\gamma_{obs.}$ (dyne/cm)</th>
<th>$\Delta %$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$68.20(T_1)$</td>
<td>90.24</td>
<td>9.76</td>
<td>0.00</td>
<td>11.78</td>
<td>12.05</td>
<td>-2.49</td>
</tr>
<tr>
<td>$68.42$</td>
<td>89.18</td>
<td>10.82</td>
<td>0.00</td>
<td>10.30</td>
<td>10.89</td>
<td>-5.99</td>
</tr>
<tr>
<td>$77.34(T_3)$</td>
<td>85.22</td>
<td>13.52</td>
<td>1.26</td>
<td>8.73</td>
<td>8.91</td>
<td>-2.02</td>
</tr>
</tbody>
</table>

### Methane

<table>
<thead>
<tr>
<th>$T^\circ K$</th>
<th>1st $%$</th>
<th>2nd $%$</th>
<th>3rd $%$</th>
<th>$\gamma_{calc.}$ (dyne/cm)</th>
<th>$\gamma_{obs.}$ (dyne/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$60.65(T_1)$</td>
<td>90.23</td>
<td>8.75</td>
<td>0.00</td>
<td>17.14</td>
<td>18.20</td>
</tr>
<tr>
<td>$69.67$</td>
<td>89.50</td>
<td>10.49</td>
<td>0.00</td>
<td>15.30</td>
<td>18.24</td>
</tr>
<tr>
<td>$111.67(T_3)$</td>
<td>87.09</td>
<td>11.91</td>
<td>1.00</td>
<td>13.91</td>
<td>13.70</td>
</tr>
<tr>
<td>$123.15$</td>
<td>84.34</td>
<td>14.26</td>
<td>1.40</td>
<td>15.73</td>
<td>13.41</td>
</tr>
</tbody>
</table>

### Benzene

<table>
<thead>
<tr>
<th>$T^\circ K$</th>
<th>1st $%$</th>
<th>2nd $%$</th>
<th>3rd $%$</th>
<th>$\gamma_{calc.}$ (dyne/cm)</th>
<th>$\gamma_{obs.}$ (dyne/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$278.68(T_1)$</td>
<td>89.60</td>
<td>9.61</td>
<td>0.79</td>
<td>37.04</td>
<td>39.05</td>
</tr>
<tr>
<td>$295.15$</td>
<td>88.38</td>
<td>10.77</td>
<td>0.85</td>
<td>34.31</td>
<td>28.36</td>
</tr>
<tr>
<td>$328.15$</td>
<td>85.84</td>
<td>12.88</td>
<td>1.28</td>
<td>29.98</td>
<td>24.44</td>
</tr>
<tr>
<td>$353.25(T_3)$</td>
<td>83.39</td>
<td>15.02</td>
<td>1.39</td>
<td>36.15</td>
<td>21.24</td>
</tr>
</tbody>
</table>

### Chlorine

<table>
<thead>
<tr>
<th>$T^\circ K$</th>
<th>1st $%$</th>
<th>2nd $%$</th>
<th>3rd $%$</th>
<th>$\gamma_{calc.}$ (dyne/cm)</th>
<th>$\gamma_{obs.}$ (dyne/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$172.12(T_1)$</td>
<td>96.40</td>
<td>3.60</td>
<td>0.00</td>
<td>57.24</td>
<td>39.2</td>
</tr>
<tr>
<td>$195.15$</td>
<td>95.97</td>
<td>4.03</td>
<td>0.00</td>
<td>43.24</td>
<td>35.1</td>
</tr>
<tr>
<td>$239.05(T_3)$</td>
<td>94.88</td>
<td>4.70</td>
<td>0.42</td>
<td>33.60</td>
<td>25.8</td>
</tr>
</tbody>
</table>

### Bromine

<table>
<thead>
<tr>
<th>$T^\circ K$</th>
<th>1st $%$</th>
<th>2nd $%$</th>
<th>3rd $%$</th>
<th>$\gamma_{calc.}$ (dyne/cm)</th>
<th>$\gamma_{obs.}$ (dyne/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$265.85(T_1)$</td>
<td>94.71</td>
<td>5.29</td>
<td>0.00</td>
<td>57.51</td>
<td>46.4</td>
</tr>
<tr>
<td>$285.15$</td>
<td>94.23</td>
<td>5.77</td>
<td>0.00</td>
<td>52.70</td>
<td>41.5</td>
</tr>
<tr>
<td>$299.15$</td>
<td>93.73</td>
<td>6.27</td>
<td>0.00</td>
<td>46.99</td>
<td>35.2</td>
</tr>
</tbody>
</table>

### Iodine

<table>
<thead>
<tr>
<th>$T^\circ K$</th>
<th>1st $%$</th>
<th>2nd $%$</th>
<th>3rd $%$</th>
<th>$\gamma_{calc.}$ (dyne/cm)</th>
<th>$\gamma_{obs.}$ (dyne/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$387.30(T_1)$</td>
<td>91.92</td>
<td>8.08</td>
<td>0.00</td>
<td>72.79</td>
<td>...</td>
</tr>
<tr>
<td>$415.15$</td>
<td>92.42</td>
<td>8.58</td>
<td>0.00</td>
<td>66.76</td>
<td>...</td>
</tr>
<tr>
<td>$457.50$</td>
<td>87.89</td>
<td>11.13</td>
<td>0.88</td>
<td>60.13</td>
<td>...</td>
</tr>
</tbody>
</table>
Discussion

Davies\(^5\) shows that when a surface is formed, the molecules in the surface layer have a different environment on the side of the vapor phase against that of the bulk liquid in which the molecules have other liquid molecules as the nearest neighbors. When compared with bulk liquid there is a new possibility of randomness in that a molecule may occupy a position either in the immediately subjacent bulk phase or in the surface. These two possibilities will give rise to an entropy increase of approximately R\(\ln 2\), i.e., 1.4 e.u., this being a standard molar entropy change associated with surface formation.

The excess molar surface entropies of the top surface layer, \(\Delta S_1\), of argon, nitrogen and methane are nearly equal to the value, R\(\ln 2\).

However, for halogens and for complex molecules like benzene, ethylenechloride and carbon tetrachloride the values, \(\Delta S_1\) are generally greater than R\(\ln 2\). It is considered that the molecules acquire, as they come to the top surface layer, different molecular degrees of freedom, i.e. rotational degrees of freedom, from their original state in the bulk liquid.

For ammonia and water, the calculated values of \(\Delta S_1\) are comparatively small. It is the result from the assumption that molecules on the top surface layer orientate to some degrees.

Generally speaking, \(\Delta S_1\) decreases with increasing temperature. But for liquids of halogens and of complex molecules, \(\Delta S_1\) increases with increasing temperatures for a low liquid temperature range with a diminishing rate, \(\Delta S_1\) eventually decreasing to zero at the critical point. This is understood as the result that due to the change of molecular degrees of freedom, the molar entropy for the top surface layer increases faster than for the bulk liquid for the low liquid temperature range.

\(\Delta S_1\), \(\Delta S_2\), increase in general, with increasing temperature but they must also become zero at the critical point since the interface between liquid and vapor disappears.

The calculations indicate that most of the entropy of surface formation is derived from the top surface layer.

This is illustrated from the percent contribution by each surface tension.

References

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