ON THE THEORY OF LIQUIDS—V.

BY T. S. WHEELER,

Royal Institute of Science, Bombay.

Received October 19, 1935.

1. Introduction.

The theory under discussion in this series of papers1 is a modification and extension of Edser's theory2; it considers a liquid as composed of a number of simultaneously attracting and repelling force centres or molecules, each of which vibrates within a spherical space of diameter $\sigma$, which is kept free from other molecules by the thermal motion of the occupying molecule. This, it should be emphasised, represents a statistical effect; occasionally a molecule will be associated with a greater or even a smaller space, but usually there will be no other molecules within the associated space of diameter $\sigma$, and outside it there will be uniform distribution of molecular centres. Near the melting-point, the translational motion of a molecule will be small compared with the vibratory motion within its spherical space.

$\sigma$ is considered to vary with the temperature, and not as Edser assumed to be independent of it. It is calculated by supposing the spaces are closely packed so that it is related to $V$ by the equation

$$N\sigma^3 = V\sqrt{2} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

It is also assumed that $\sigma$, while it varies with temperature, is relatively independent of small alterations in other variables; for example, it is assumed that

$$\left(\frac{d\sigma}{dT}\right)_V = \left(\frac{d\sigma}{dT}\right)_\rho \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (2)$$

In other words, the space which it keeps clear by its thermal motion is an intrinsic property of a molecule at a given temperature.

A number of formulæ for various properties of liquids have been developed in the previous papers. In Parts I, II, III, the equations were of the type which related various properties of a liquid one to another, but one property of a liquid, say the density, had to be known before the remainder could be calculated. In Part IV, equations were deduced for the

---


forces on a particle vibrating in a spherical space under the influence of attractive and repulsive forces between the particle, and uniformly distributed matter outside the spherical space.

The object of this paper, which is intended to be the last of the series, is to give a summarised presentation of the theory, with an outline of the derivation and application of the principal equations, and to show how with the aid of the equations derived in Part IV, the properties of a liquid could be calculated, if the temperature, and the fundamental properties of a molecule, the forces which it generates, are known.

2. General Considerations.

It is assumed that we are dealing with a liquid of low vapour pressure near the melting-point. The translational motions of the molecules are neglected, and each molecule is taken to be vibrating within its associated spherical space of diameter \( \sigma \). It attracts and repels other centres by forces which are given respectively by \( \frac{\mu}{r^m} \) and \( \frac{\lambda}{r^n} \). It is assumed that when the molecule is at the centre of its associated space, the effect of the short-range repulsive force is negligible in comparison with that of the long-range attractive force. The former force comes into play only when the molecule is displaced towards the circumference of its space.

For a few substances \( \mu \) and \( m \) can be calculated from the gaseous second virial coefficient by the method of Lennard-Jones (See Part II, p. 108). For normal organic liquids, \( m = 11 \), and \( \mu \) can be related to the parachor \( P \), which can be calculated from the atomic values without any direct measurement (See Part II, p. 107). Initially we will show how a number of properties of a liquid can be quantitatively deduced from \( T, \sigma \) and \( \mu \) and \( m \), or \( P \), and we will then indicate how \( \sigma \) could be calculated from a knowledge of \( T, \mu, \lambda, m \) and \( n \).

3. Surface Tension.

Edser (loc. cit., p. 62) has shown that the surface tension of a liquid is given by

\[
\gamma = \frac{\pi \mu N^2}{8(m - 5)\sqrt{m-5}} \ldots \ldots \ldots \ldots \ldots (3)
\]

It should be noted that in deriving \( \gamma \), the average effect of a molecule over a reasonably long time interval is obtained by assuming that its mean position is the centre of its spherical space, and that its vibrations can here be neglected.
Inserting (1) in (3) we have
\[ \gamma = \frac{\pi \mu}{4(m - 5)\sigma^{m+1}} \]
in which all the quantities are known.
Alternatively we can combine (1) and (3) to give
\[ \gamma = \frac{\pi \mu}{4(m - 5)\sigma^{m+1}} \frac{N^{\frac{m+1}{3}}}{V^{\frac{m+1}{3}}} \]
\[ = \frac{P^{\frac{m+1}{3}}}{V^{\frac{m+1}{3}}} \]
where
\[ \frac{m+1}{3} \]
\[ P^{\frac{m+1}{3}} = \frac{\pi \mu}{4(m - 5)\sigma^{m+1}} \frac{N^{\frac{m+1}{3}}}{V^{\frac{m+1}{3}}} \]
If we put \( m = 11 \), (6) becomes
\[ \gamma = \frac{P^4}{V^4} \]
where
\[ P^4 = \frac{\pi \mu N^4}{96} \]
that is
\[ \mu = \frac{96 P^4}{\pi N^4} \]
(8) is the parachor law for low vapour pressures. Since the parachor for normal liquids can be calculated from the molecular structure, (10) enables us to calculate \( \mu \) for such liquids.

Table I gives values of \( \mu \) and \( m \) for some liquefied gases calculated from the second virial coefficient (Part II, p. 108), and also values of \( \mu \) for some

<table>
<thead>
<tr>
<th>Substance</th>
<th>( m )</th>
<th>( \mu )</th>
<th>Substance</th>
<th>( P^4 )</th>
<th>( \mu \times 10^{18} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>7</td>
<td>( 5.77 \times 10^{-66} )</td>
<td>(C(_2)H(_5))(_2)O</td>
<td>210.2</td>
<td>4.43</td>
</tr>
<tr>
<td>H(_2)</td>
<td>8</td>
<td>( 2.33 \times 10^{-66} )</td>
<td>(CH(_4))(_2)CO</td>
<td>160.2</td>
<td>1.49</td>
</tr>
<tr>
<td>Ne</td>
<td>7</td>
<td>( 2.55 \times 10^{-59} )</td>
<td>C(<em>6)H(</em>{14}) ((n))</td>
<td>268.2</td>
<td>11.7</td>
</tr>
<tr>
<td>Ar</td>
<td>8</td>
<td>( 1.41 \times 10^{-65} )</td>
<td>CHCl(_3)</td>
<td>184.8</td>
<td>2.64</td>
</tr>
<tr>
<td>N(_2)</td>
<td>8</td>
<td>( 2.02 \times 10^{-65} )</td>
<td>CCl(_4)</td>
<td>222.0</td>
<td>5.52</td>
</tr>
<tr>
<td>C(_6)H(_6)</td>
<td></td>
<td></td>
<td></td>
<td>207.1</td>
<td>4.16</td>
</tr>
</tbody>
</table>

* Calculated from molecular structure.
normal organic liquids calculated by means of (10) (Part II, p. 107). These values are used throughout this paper. Table II shows the application

<table>
<thead>
<tr>
<th>Substance</th>
<th>T</th>
<th>$\sigma \times 10^8$</th>
<th>$\gamma'_{(4)}$</th>
<th>$\gamma_{(ob.)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>1.5</td>
<td>4.02</td>
<td>0.33</td>
<td>0.35</td>
</tr>
<tr>
<td>H$_2$</td>
<td>15.0</td>
<td>3.97</td>
<td>2.5</td>
<td>2.8</td>
</tr>
<tr>
<td>Ne</td>
<td>24.7</td>
<td>3.88</td>
<td>5.9</td>
<td>5.6</td>
</tr>
<tr>
<td>Ar</td>
<td>85.0</td>
<td>4.03</td>
<td>13.2</td>
<td>13.2</td>
</tr>
<tr>
<td>N$_2$</td>
<td>70.0</td>
<td>4.28</td>
<td>10.9</td>
<td>10.5</td>
</tr>
</tbody>
</table>

of (4) to those substances for which $\mu$ and $m$ have been calculated from the second virial coefficient (Part II, p. 110); (8) is already known to hold with fair accuracy for normal liquids at temperatures of low vapour pressure.

4. Internal Thermal Pressure.

In Part III (p. 798), the thermal pressure on a unit plane in the liquid, which is the product of the number of molecular spaces in contact with the plane, the frequency of vibration of the corresponding molecules (see section 7) and the change in momentum in each vibration towards the plane due to the repulsive forces, is shown to be given by the equation,

$$ p_T = \frac{2}{\sqrt{3}} \cdot \frac{kT}{\beta \sigma^3} $$

where $\beta$ is the fractional amplitude of vibration.

5. Cohesive Pressure.

Edser (loc. cit., p. 58) has shown that the cohesive pressure $K$ of a liquid is given by

$$ K = \frac{2\pi \mu N^2}{3(m-4)\sigma^{m-4}V^2} $$

the terms due to the repulsive force being neglected. Substituting (1) in (12) we have

$$ K = \frac{4\pi \mu}{3(m-4)\sigma^{m+2}} $$

in which all the quantities are known.

Inserting (10) and (1) in (12) and putting $m = 11$, we obtain

$$ K = \frac{32}{7\sigma} \cdot \frac{P^4}{V^4} $$
The quantities in (13) and (14) are all known, \( V \) being at once derived from \( \sigma \) by means of (1). Table III shows the application of (13) and (14). The values obtained with (14) are of the same order as those deduced by other methods. (See Hildebrand, Solubility, 1924, p. 99).

**Table III.**

<table>
<thead>
<tr>
<th>Substance</th>
<th>( T )</th>
<th>( \sigma \times 10^8 )</th>
<th>( K ) ats. (13)</th>
<th>Substance</th>
<th>( T )</th>
<th>( \sigma \times 10^8 )</th>
<th>( K ) ats. (14)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>1.0</td>
<td>4.02</td>
<td>29</td>
<td>(C\textsubscript{2}H\textsubscript{2})\textsubscript{2}O</td>
<td>273</td>
<td>6.16</td>
<td>1415</td>
</tr>
<tr>
<td>H\textsubscript{2}</td>
<td>13.9</td>
<td>3.92</td>
<td>280</td>
<td>(CH\textsubscript{3})\textsubscript{2}CO</td>
<td>293</td>
<td>5.55</td>
<td>1840</td>
</tr>
<tr>
<td>Ne</td>
<td>24.5</td>
<td>3.35</td>
<td>660</td>
<td>C\textsubscript{6}H\textsubscript{14}(n)</td>
<td>273</td>
<td>6.64</td>
<td>1350</td>
</tr>
<tr>
<td>Ar</td>
<td>63.1</td>
<td>4.02</td>
<td>1320</td>
<td>CHCl\textsubscript{3}</td>
<td>288</td>
<td>5.71</td>
<td>2250</td>
</tr>
<tr>
<td>N\textsubscript{2}</td>
<td>63.1</td>
<td>4.23</td>
<td>1140</td>
<td>CCl\textsubscript{4}</td>
<td>273</td>
<td>6.02</td>
<td>2300</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C\textsubscript{6}H\textsubscript{6}</td>
<td>270</td>
<td>5.87</td>
<td>2410</td>
</tr>
</tbody>
</table>

6. *Fractional Amplitude of Vibration.*

At equilibrium the thermal and cohesive pressures are equal, since the external pressure can be neglected in comparison; equating (11) and (13) we have

\[
\beta = \frac{\sqrt{3}(m - 4)\sigma^{m-1}kT}{2\pi\mu}
\]

or with (1) and (10), putting \( m = 11 \),

\[
\beta = \frac{7}{48\alpha^2} \cdot \frac{\sqrt{3}kT}{P^4} \cdot \frac{V^4}{P^4}
\]

\( \beta \) can be calculated from (15) and (16). Further, differentiation of (15) with respect to \( T \) gives

\[
\frac{d\beta}{dT} = \frac{\beta}{T} + \frac{(m-1)\beta}{\sigma} \frac{d\sigma}{dT}
\]

\[
= \frac{\beta}{T} + \frac{(m-1)\beta}{3}
\]

As \( \sigma \) is assumed to be known at each temperature, \( \alpha \) is known and hence from (18), \( \frac{d\beta}{dT} \) can be calculated, when \( \beta \) has been determined. Table IV shows the application of (15) and (16) to calculate \( \beta \) (Cf. Tables 1 and 2, Part III). The values are of the same order as those obtained for \( \beta_{m,\phi} \) in solids from specific heat and other data. Values for \( \frac{d\beta}{dT} \) are also given; it is usually about two-thirds of \( \alpha \).
On the Theory of Liquids—V

Table IV.

<table>
<thead>
<tr>
<th>Substance</th>
<th>T</th>
<th>$\sigma \times 10^8$</th>
<th>$\alpha$</th>
<th>$\beta$ (15)</th>
<th>$\frac{d\beta}{dT}$ (18)</th>
<th>Substance</th>
<th>T</th>
<th>$\sigma \times 10^8$</th>
<th>$\alpha$</th>
<th>$\beta$ (16)</th>
<th>$\frac{d\beta}{dT}$ (18)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>1.0</td>
<td>4.02</td>
<td>..</td>
<td>0.083</td>
<td>0.083</td>
<td>(C$_2$H$_5$)$_2$O</td>
<td>273</td>
<td>6.17</td>
<td>0.0015</td>
<td>0.128</td>
<td>0.0011</td>
</tr>
<tr>
<td>H$_2$</td>
<td>13.9</td>
<td>3.92</td>
<td>0.012</td>
<td>0.128</td>
<td>0.012</td>
<td>(CH$_3$)$_2$CO</td>
<td>293</td>
<td>5.55</td>
<td>0.0014</td>
<td>0.145</td>
<td>0.0012</td>
</tr>
<tr>
<td>Ne</td>
<td>24.5</td>
<td>3.35</td>
<td>0.014</td>
<td>0.153</td>
<td>0.011</td>
<td>C$_6$H$_4$(n)</td>
<td>273</td>
<td>6.64</td>
<td>0.0014</td>
<td>0.106</td>
<td>0.0009</td>
</tr>
<tr>
<td>Ar</td>
<td>83.1</td>
<td>4.02</td>
<td>0.0044</td>
<td>0.151</td>
<td>0.0034</td>
<td>CHCl$_3$</td>
<td>288</td>
<td>5.71</td>
<td>0.0012</td>
<td>0.107</td>
<td>0.0008</td>
</tr>
<tr>
<td>N$_2$</td>
<td>63.1</td>
<td>4.23</td>
<td>0.0048</td>
<td>0.114</td>
<td>0.0031</td>
<td>CCl$_4$</td>
<td>273</td>
<td>6.02</td>
<td>0.0012</td>
<td>0.085</td>
<td>0.0007</td>
</tr>
</tbody>
</table>

7. Frequency of Vibration.

As shown in Part III (p. 797), the frequency of vibration of a molecule within its spherical space is given by

$$\nu = \frac{1}{\sqrt{2\pi}} \sqrt{\frac{kT}{m}} \frac{1}{\beta \sigma}$$  \hspace{1cm} (19)

which with (15) gives

$$\nu = \frac{\sqrt{\frac{2\pi}{\mu}}}{\sqrt[3]{(m-4)\sigma^m \sqrt{m}} \sqrt{kT}}$$  \hspace{1cm} (20)

in which all the quantities are known. If we put $m = 11$, (20) on insertion of (1) and (10) gives

$$\nu = \frac{8 \sqrt{6} \frac{D^4}{7 \sqrt{\pi} V^4}}{\sqrt{\sqrt{m}hT}}$$  \hspace{1cm} (21)

Table V shows the application of (20) and (21). It should be noted that if in (19) we put $\beta = 0.1$, the equation reduces to Lindemann's equation for the frequency at the melting-point (See Part III, p. 798).

Table V.

<table>
<thead>
<tr>
<th>Substance</th>
<th>T</th>
<th>$\sigma \times 10^8$</th>
<th>$\nu$ (20)</th>
<th>Substance</th>
<th>T</th>
<th>$\sigma \times 10^8$</th>
<th>$\nu$ (21)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>..</td>
<td>1.0</td>
<td>4.02</td>
<td>5.44$\times 10^{11}$</td>
<td>(C$_2$H$_5$)$_2$O</td>
<td>273</td>
<td>6.16</td>
</tr>
<tr>
<td>H$_2$</td>
<td>..</td>
<td>13.9</td>
<td>3.92</td>
<td>1.92$\times 10^{12}$</td>
<td>(CH$_3$)$_2$CO</td>
<td>293</td>
<td>5.55</td>
</tr>
<tr>
<td>Ne</td>
<td>..</td>
<td>24.5</td>
<td>3.35</td>
<td>7.81$\times 10^{11}$</td>
<td>C$_6$H$_4$(n)</td>
<td>273</td>
<td>6.64</td>
</tr>
<tr>
<td>Ar</td>
<td>..</td>
<td>83.1</td>
<td>4.02</td>
<td>8.64$\times 10^{11}$</td>
<td>CHCl$_3$</td>
<td>288</td>
<td>5.71</td>
</tr>
<tr>
<td>N$_2$</td>
<td>..</td>
<td>63.1</td>
<td>4.23</td>
<td>1.13$\times 10^{12}$</td>
<td>CCl$_4$</td>
<td>273</td>
<td>6.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C$_6$H$_6$</td>
<td>279</td>
<td>5.87</td>
</tr>
</tbody>
</table>
8. Viscosity.

In Part III (p. 802), it has been shown that

\[ \eta = \frac{8R^4}{3 \sqrt{\pi N}} \beta \sigma^5 \]

which with (15) gives

\[ \eta = \frac{16 \sqrt{\pi}}{3 \sqrt{3(m-4)}} \frac{\mu}{\sigma^{m+1}} \frac{M^4}{R^4 T^4} \]

Putting \( m = 11 \), and inserting (1) and (10), (23) becomes

\[ \eta = \frac{128 M^4}{7 \sqrt{3 \pi}} \frac{P^4}{R^4 T^4} \]

Table VI shows the application of (23) and (24). For substances for which \( \eta \) is known, the agreement is fair, particularly when allowance is made for the fact that for some of the substances, data near the melting-point are not available.

**TABLE VI.**

<table>
<thead>
<tr>
<th>Substance</th>
<th>T [C]</th>
<th>( \sigma \times 10^8 )</th>
<th>( \eta ) (23)</th>
<th>( \eta ) (obs.)</th>
<th>Substance</th>
<th>T [C]</th>
<th>V</th>
<th>( \eta ) (24)</th>
<th>( \eta ) (obs.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>2.3</td>
<td>4.02</td>
<td>0.0002</td>
<td>0.0003</td>
<td>(C(_2)H(_5))(_2)O</td>
<td>198</td>
<td>90.7</td>
<td>0.011</td>
<td>0.009</td>
</tr>
<tr>
<td>H(_2)</td>
<td>13.9</td>
<td>3.92</td>
<td>0.0006</td>
<td></td>
<td>(CH(_3)(_2))CO</td>
<td>200</td>
<td>64.9</td>
<td>0.013</td>
<td>0.013</td>
</tr>
<tr>
<td>Ne</td>
<td>24.5</td>
<td>3.35</td>
<td>0.0029</td>
<td></td>
<td>C(_6)H(_4) (a)</td>
<td>273</td>
<td>127.0</td>
<td>0.007</td>
<td>0.004</td>
</tr>
<tr>
<td>Ar</td>
<td>83.1</td>
<td>4.02</td>
<td>0.0053</td>
<td></td>
<td>CHCl(_3)</td>
<td>263</td>
<td>77.2</td>
<td>0.014</td>
<td>0.008</td>
</tr>
<tr>
<td>N(_2)</td>
<td>68.1</td>
<td>4.23</td>
<td>0.0046</td>
<td></td>
<td>CCl(_4)</td>
<td>273</td>
<td>94.2</td>
<td>0.015</td>
<td>0.013</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C(_6)H(_6)</td>
<td>279</td>
<td>87.3</td>
<td>0.011</td>
<td>0.008</td>
</tr>
</tbody>
</table>


Edser\(^3\) has shown that the internal work of evaporation is given by the formula

\[ A_i = \frac{2\pi \mu N^2}{3(m-4)V \sigma^{m-4}} \]

which inserting (1) gives,

\[ A_i = \frac{2 \sqrt{2 \pi \mu N}}{3(m-4)\sigma^{m-1}} \]

(26), when \( m \) is put = 11, becomes, if (1) and (10) be inserted,

\[ A_i = \frac{32 P^4}{7 \sigma V^3} \]

---

\(^3\) *Loc. cit.*, p. 67.
On the Theory of Liquids—V


The Gibbs-Helmholtz equation gives

\[ I_i = \Lambda_i - T \left( \frac{\delta \Lambda}{\delta T} \right)_V \]

From (25) we have

\[ \left( \frac{\delta \Lambda}{\delta T} \right)_V = - \frac{(m-4)\Lambda}{\sigma} \left( \frac{\delta \sigma}{\delta T} \right)_V \]

which with the assumption contained in (2) gives

\[ \left( \frac{\delta \Lambda}{\delta T} \right)_V = - \frac{(m-4)\Lambda}{\sigma} \left( \frac{\delta \sigma}{\delta T} \right)_V \]

since

\[ a = \frac{1}{V} \left( \frac{\delta V}{\delta T} \right)_P \]

and hence from (1)

\[ \frac{3}{\sigma} \left( \frac{\delta \sigma}{\delta T} \right)_P \]

Hence from (28) and (31),

\[ I_i = \Lambda_i \left[ 1 + \frac{T(m-4)a}{3} \right] \]

where \( \Lambda_i \) is given by (26). From (27) we have

\[ I_i = \frac{32 \, P^4}{7 \sigma} \left[ 1 + \frac{7Ta}{3} \right] \]

Table VII shows the application of (34) and (35). The agreement with (34) is better than with (35).


In Part I (p. 528), the application of the following three specific heat equations is discussed:

(a) \( C_{pV} - C_{vV} = - \left( \frac{\delta L_i}{\delta T} \right)_P \)

\[ = \Lambda_i a \left[ 1 + \frac{T(m-1)(m-4)a}{9} \right] \]

(b) \( C_{pV} - C_{vV} = - \left( \frac{\delta L_i}{\delta T} \right)_P \)

\[ = \left( \frac{\delta L_i}{\delta T} \right)_P \frac{\delta V}{\delta T}_P \]

\[ = \Lambda_i a \left( 1 + \frac{(m-4)aT}{3} \right) \]

\[ ^4 \text{Cf. Tyrer, Zeit. Phys. Chem., 1914, 87, 177.} \]
### Table VII.

<table>
<thead>
<tr>
<th>Substance</th>
<th>$T$</th>
<th>$\sigma \times 10^8$</th>
<th>$\alpha$</th>
<th>$A_i$ cals. (26)</th>
<th>$L_i$ cals. (34)</th>
<th>$L_i$ cals. (obs.)</th>
<th>Substance</th>
<th>$T$</th>
<th>$\sigma \times 10^8$</th>
<th>$\alpha$</th>
<th>$A_i$ K-cals. (27)</th>
<th>$L_i$ K-cals. (35)</th>
<th>$L_i$ K-cals. (obs.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>1.75</td>
<td>4.02</td>
<td>.</td>
<td>19</td>
<td>19</td>
<td>19</td>
<td>(C$_2$H$_5$)$_2$O</td>
<td>273</td>
<td>6.16</td>
<td>0.0015</td>
<td>3.43</td>
<td>6.72</td>
<td>6.28</td>
</tr>
<tr>
<td>H$_2$</td>
<td>15.0</td>
<td>3.97</td>
<td>0.012</td>
<td>182</td>
<td>201</td>
<td>189</td>
<td>(C$_2$H$_3$)CO</td>
<td>293</td>
<td>5.55</td>
<td>0.0014</td>
<td>3.27</td>
<td>6.40</td>
<td>7.06</td>
</tr>
<tr>
<td>Ar</td>
<td>87.1</td>
<td>4.05</td>
<td>0.0046</td>
<td>845</td>
<td>1326</td>
<td></td>
<td>C$_6$H$_4$(n)</td>
<td>273</td>
<td>6.64</td>
<td>0.0014</td>
<td>4.15</td>
<td>7.82</td>
<td>7.11</td>
</tr>
<tr>
<td>N$_2$</td>
<td>63.1</td>
<td>4.23</td>
<td>0.0048</td>
<td>891</td>
<td>1250</td>
<td>1330</td>
<td>CHCl$_3$</td>
<td>288</td>
<td>5.71</td>
<td>0.0012</td>
<td>4.33</td>
<td>7.87</td>
<td>6.98</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>CCl$_4$</td>
<td>273</td>
<td>6.02</td>
<td>0.0012</td>
<td>5.24</td>
<td>9.26</td>
<td>7.45</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C$_6$H$_6$</td>
<td>279</td>
<td>5.87</td>
<td>0.0012</td>
<td>5.09</td>
<td>9.07</td>
<td>7.71</td>
</tr>
</tbody>
</table>

### Table VIII.

<table>
<thead>
<tr>
<th>Substance</th>
<th>$T$</th>
<th>$V$</th>
<th>$\alpha$</th>
<th>$L_i$ ergs. (34)</th>
<th>$c$ (44)</th>
<th>Substance</th>
<th>$T$</th>
<th>$V$</th>
<th>$\alpha$</th>
<th>$L_i$ ergs. (35)</th>
<th>$c$ (44)</th>
<th>$c$ (obs.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>15.0</td>
<td>26.3</td>
<td>0.012</td>
<td>8.43 $\times 10^9$</td>
<td>5.61 $\times 10^{-10}$</td>
<td>(C$_2$H$_5$)$_2$O</td>
<td>273</td>
<td>100.5</td>
<td>0.0015</td>
<td>2.81 $\times 10^{11}$</td>
<td>14.7 $\times 10^{-11}$</td>
<td>15.0 $\times 10^{-11}$</td>
</tr>
<tr>
<td>Ar</td>
<td>87.1</td>
<td>28.5</td>
<td>0.0046</td>
<td>5.45 $\times 10^{10}$</td>
<td>2.10 $\times 10^{-10}$</td>
<td>(C$_2$H$_3$)CO</td>
<td>293</td>
<td>73.3</td>
<td>0.0014</td>
<td>2.68 $\times 10^{11}$</td>
<td>11.3 $\times 10^{-11}$</td>
<td>12.4 $\times 10^{-11}$</td>
</tr>
<tr>
<td>N$_2$</td>
<td>63.1</td>
<td>32.0</td>
<td>0.0048</td>
<td>5.24 $\times 10^{10}$</td>
<td>1.85 $\times 10^{-10}$</td>
<td>C$_6$H$_4$(n)</td>
<td>273</td>
<td>127.0</td>
<td>0.0014</td>
<td>3.28 $\times 10^{11}$</td>
<td>14.8 $\times 10^{-11}$</td>
<td>12.5 $\times 10^{-11}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>CHCl$_3$</td>
<td>288</td>
<td>79.8</td>
<td>0.0012</td>
<td>3.30 $\times 10^{11}$</td>
<td>8.4 $\times 10^{-11}$</td>
<td>9.7 $\times 10^{-11}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>CCl$_4$</td>
<td>273</td>
<td>94.2</td>
<td>0.0012</td>
<td>3.88 $\times 10^{11}$</td>
<td>7.9 $\times 10^{-11}$</td>
<td>9.0 $\times 10^{-11}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C$_6$H$_6$</td>
<td>279</td>
<td>87.3</td>
<td>0.0012</td>
<td>3.80 $\times 10^{12}$</td>
<td>7.7 $\times 10^{-11}$</td>
<td>8.2 $\times 10^{-11}$</td>
</tr>
</tbody>
</table>
On the Theory of Liquids—V 475

\[ (c) \ C_{vi} - C_{vg} = \left( \frac{\delta L_i}{\delta T} \right)_{V} \ldots \ldots \ldots (42) \]

\[ = \frac{A_{i}a^{2}T(m-4)^{2}}{9} \ldots \ldots \ldots (43) \]

As Tables II and III (Part I) show, the agreement with \( m, 9 \) to 11 between the observed and calculated values is moderately good, particularly when it is remembered that the fundamental equations, (36), (38) and (42) are only approximately valid. In these calculations (4) was used to replace \( \mu \) by \( \gamma \).

12. Compressibility.

The compressibility of a normal liquid\(^5\) is given by

\[ c = \frac{TaV}{L_i} \ldots \ldots \ldots \ldots \ldots (44) \]

Table VIII shows values of \( c \) calculated from (44) using values of \( L_i \), derived from (34) or (35). For those substances for which \( c \) has been measured, the agreement between the calculated and observed values is satisfactory.

13. Vapour Pressure.

A vapour-pressure equation has also been derived (Part III, p. 803) but the results obtained are only approximate and it need not further be discussed here.

14. Direct Calculation of \( \sigma \).

As shown in Part IV, the total work done by the repulsive and attractive forces as a molecule passes from the centre of its spherical space to a distance \( x \) from that centre is given by

\[ \bar{W}_1 = 4 \sqrt{2} \pi \left( \frac{\mu m}{(m-1)\sigma^{m-1}} - \frac{\lambda \bar{n}}{(n-1)\sigma^{n-1}} \right) \ldots \ldots (45) \]

where

\[ \bar{m} = \frac{X^{-(m-5)} - Y^{-(m-5)}}{2 \left( \frac{x}{\sigma} \right)^{m-5} (m-5)} + \frac{X^{-(m-4)} + Y^{-(m-4)}}{2(m-4) (m-3)} - \frac{1}{(m-4)} \ldots \ldots (46) \]

and \( \bar{n} \) corresponds to \( \bar{m} \).

In (46)

\[ X = 1 - \frac{x}{\sigma} \ldots \ldots \ldots \ldots \ldots (47) \]

and

\[ Y = 1 + \frac{x}{\sigma} \ldots \ldots \ldots \ldots \ldots (48) \]

The equilibrium equation is

\[ \frac{1}{2} kT = -4 \sqrt{2} \pi \left( \frac{\mu m}{(m-1)\sigma^{m-1}} - \frac{\lambda \bar{n}}{(n-1)\sigma^{n-1}} \right) \ldots \ldots (49) \]

The value of \( \frac{x}{\sigma} \) which satisfies this equation is \( = \beta/2 \).

From (15) we have

\[
\sigma = C \beta^{(m-1)}
\]

where C is a constant and insertion of (50) in (49), gives an equation in \( \beta \) which can be solved by graphical methods when \( \mu, \lambda, m, n, \) and \( T \) are known.

The results given in the previous portion of this paper indicate that \( \mu \) and \( m \) can be calculated from the second virial coefficient and applied to the liquid state. Attempts to use the corresponding values of \( \lambda \) and \( n \) in (49) led to values of \( \beta \) which were much too large. The repulsive force though negligible when the molecule is at the centre of its spherical space appears to increase when the molecule is displaced from the centre of the space much more rapidly than the corresponding repulsive force in the gaseous state. Until some means have been found for determining \( \lambda \) and \( n \) for the liquid state, it will be impossible to evaluate (49) and thus directly determine \( \beta \) and thence \( \alpha \) by means of (15).

**NOTATION ADOPTED.**

\( A_i \) Internal work of evaporation. Work done against van der Waals forces in evaporating isothermally 1 g.-mol. of a liquid to the state of infinitely dilute vapour.

\( c \) Compressibility.

\( C_{pl} \) Molecular heat of the liquid at constant pressure.

\( C_{pv} \) Molecular heat of the liquid at constant volume.

\( C_{v} \) Molecular heat of the liquid vapour at constant volume.

\( K \) Internal pressure.

\( k \) Boltzmann's constant.

\( L_i \) Internal latent heat of vapourisation.

\( m \) Index of the power of the inverse distance expressing the variation of the attractive force between two molecules.

\( M \) Molecular weight.

\( m \) Mass of a molecule. See also (46).

\( n \) Index for the repulsive force.

\( N \) Number of molecules in 1 g.-mol.

\( P \) Parachor constant.

\( p \) External pressure.

\( p_i \) Internal thermal pressure.

\( R \) Gas constant.

\( r \) Distance between two molecules.

\( T \) Absolute temperature.

\( V \) Volume of 1 g.-mol. of the liquid in the normal state at \( T \).

\( x \) Distance a molecule is removed from the centre of its spherical space.

\( a \) Coefficient of thermal expansion of a liquid.

\( \beta \) Fractional amplitude of vibration of a molecular centre within its spherical space.

\( \eta \) Viscosity.

\( \gamma \) Surface tension.

\( \lambda \) Repulsive force coefficient.

\( \mu \) Attractive force coefficient.

\( \nu \) Frequency of vibration.

\( \sigma \) Diameter of spherical space which a molecule keeps clear around it by its thermal motion.