A NEW CORRELATION TO PREDICT CRITICAL VOLUME

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ABSTRACT

A new correlation employing parachor as the only input datum for predicting critical volume has been developed and tested. In the case of 159 organic compounds the average absolute deviation is 1.31%.

A knowledge of critical constants of substances is essential for the use of various generalized correlations for liquids and gases. The experimental determination of these constants is not simple and for this reason any method for predicting the constants should be of great value. Among the many available correlations, the method due to Lydersen predicts the critical volume with an average error of 2.3%, and that due to Das et al predicts with an average error of 1.7% according to the authors themselves. The former method employs additive group technique, originally suggested by Schuster and the latter method employs molecular weight as the input datum. Critical volume can also be estimated by critical compressibility method. In this method the values of $Z_c$, $T_c$ and $P_c$ must be either known or estimated. This method predicts critical volume with an average error of 3.6%.

The proposed method employs parachor as the input datum. Parachor can be estimated by group contribution technique employing the values listed by Reid and Sherwood. The present correlation employs the following expressions for predicting critical volume.

$$V_c = 1.4[P] + C$$  \[1\]

1. HOW THIS CORRELATION WAS DEVELOPED

Approximate relation to predict hard sphere volume, from critical volume for spherical non-polar molecules obeying the Lennard-Jones (6-12) potential is

$$b_0 = 0.75 V_c$$  \[2\]

The hard sphere volume is also related to the intermolecular distance by the following expression

$$b_0 = 1.2615 \sigma^2$$  \[3\]

* Deceased.
From Equations [2] and [3] we have

\[ V_c = \frac{1.2615}{0.75} \sigma^3 \]  

According to cell-theory, the collision diameter is related to parachor (3) as,

\[ [P] = 7.1 \times 10^{23} \varepsilon^{0.25} \sigma^{5/2} \]  

Since a gm. mole contains \(6.023 \times 10^{23}\) molecules, we have

\[ [P] = \frac{7.1 \times 10^{23} \varepsilon^{0.25} \sigma^{5/2}}{6.023 \times 10^{23}} = 1.1788 \varepsilon^{0.25} \sigma^{5/2} \]  

From Equation [6] we have

\[ \sigma^3 = \frac{[P]^{1.2}}{1.217 \varepsilon^{0.3}} \]  

From Equations [4] and [7], we have

\[ V_c = 1.382 \left[ \frac{[P]^{1.2}}{\varepsilon^{0.3}} \right] \]  

Equation [8], shows the critical volume, is directly related to parachor.

A linear relation is obtained when critical volume was plotted against parachor, for different homologous series. The slopes for all the lines was found to be 1.4 which is in close agreement with the value 1.38 of Equation [8]. The intercepts for different homologous series are given in Table 4.

As the slope is constant for different homologous series, one experimental data is sufficient to calculate the constant \(C_1\) in Equation [1], for a particular series.

Group contribution method:

Based on the data obtained above a group contribution technique has been developed. The Equation [1] can be written as

\[ V_c = A + C \]  

\(A\) and \(C\) are calculated by employing the values in Table 2.
Example: Benzene

\( A \) is calculated as follows:
- 6 Carbon atoms \( = 6 \times 12.6 = 75.6 \)
- 6 Hydrogen atoms \( = 6 \times 21.7 = 130.2 \)
- 3 Double bonds \( = 3 \times 26.74 = 80.22 \)
- 6 membered ring closure \( = 1.12 \)

\[ 287.14 \]

\( C \) is calculated as follows:
- \( C_6H_6 = (CH_3)_6 - 12H + 3 \) double bonds + ring closure
- 6 \( CH_3 \) groups \( = 6 \times -8 = -48 \)
- 12 Hydrogen atoms \( = 0 \times 12 = 0.0 \)
- 3 Double bonds \( = 3 \times 11 = +33.0 \)
- 6 membered closure \( = -15 \)

\[ V_c = A + C \]

\[ - 30 \]

Substituting the values of \( A \) and \( C \), we have

\[ V_c = 257.14 \text{ c.c./g. mole, whereas the experimental value is} \]

\[ 260.33 \text{ c.c./g. mole,} \]

Table 1 groups all the 159 compounds considered and shows the critical volume obtained from literature \((2.5)\) and compares with the calculated values. Table 2 gives different atomic contributions and group contributions to evaluate constants \( A \) and \( C \) respectively. The values given in Table 2 to evaluate constant \( C \) are applicable only to first member of each homologous series. The constant \( C \) is evaluated for the first member of homologous series and it remains the same for that series. In calculation of \( V_c \) it is only the value of \( A \) that changes from member to member in homologous series. Table 3 compares the present method with Lydersen and Das et al methods. The methods due to Lydersen\(^4\) and Das et al\(^1\) are claimed by authors to give an average error of 2.3 and 1.7\%, respectively. A comparison made in the present study considering the same number of compounds for which experimental data is available, however, gives average errors as shown in Table 3. From the table it is seen that the error involved in the present method is of the same order as Lydersen's method and the present method is better than Das et al method. However, in the case of the 159 substances considered the present method gives an average absolute error of 1.31\%.
<table>
<thead>
<tr>
<th></th>
<th>$V_n$, c.c./g mole</th>
<th>Exptl.</th>
<th>Calcd.</th>
<th>% Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Paraffins</td>
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<td></td>
</tr>
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<td>1.41</td>
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<td>475.0</td>
<td></td>
<td>2.36</td>
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<td>475.0</td>
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<td>-0.62</td>
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<td>539.5</td>
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</tbody>
</table>
### Table 1 — (contd.)

Experimental and calculated values of critical volume.

<table>
<thead>
<tr>
<th>Compound</th>
<th>V, c.c./g. mole</th>
<th>% Error</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>n-Hexadecane</strong></td>
<td>915.0</td>
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<td><strong>n-Heptadecane</strong></td>
<td>1000.0</td>
<td>0.54</td>
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<tr>
<td><strong>n-Octadecane</strong></td>
<td>1100.0</td>
<td>4.45</td>
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<td><strong>n-Nonadecane</strong></td>
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<td>0.67</td>
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<td><strong>n-Eicosane</strong></td>
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<tr>
<td><strong>Average</strong></td>
<td>10.4</td>
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</table>

2. **Mono-Olefins**

<table>
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<tr>
<th>Compound</th>
<th>V, c.c./g. mole</th>
<th>% Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethene</td>
<td>133.5</td>
<td>0.17</td>
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<tr>
<td>Propene</td>
<td>181.0</td>
<td>4.82</td>
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<tr>
<td>n-Butene</td>
<td>241.0</td>
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<td>n-Pentene</td>
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<td>-2.41</td>
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<td>n-Hexene</td>
<td>365.4</td>
<td>-2.09</td>
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<tr>
<td>n-Heptene</td>
<td>416.9</td>
<td>-0.77</td>
</tr>
<tr>
<td>n-Octene</td>
<td>468.2</td>
<td>0.32</td>
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<td>n-Nonene</td>
<td>504.9</td>
<td>2.16</td>
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<td>n-Decene</td>
<td>576.4</td>
<td>0.91</td>
</tr>
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<td><strong>Average</strong></td>
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</table>

3. **Alkynes**

<table>
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<th>Compound</th>
<th>V, c.c./g. mole</th>
<th>% Error</th>
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<td>Propyne</td>
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<td>Ethyl acetylene</td>
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<td>Propyl acetylene</td>
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<tr>
<td><strong>Average</strong></td>
<td>0.69</td>
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4. **Cyclopentanes**

<table>
<thead>
<tr>
<th>Compound</th>
<th>V, c.c./g. mole</th>
<th>% Error</th>
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</thead>
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<tr>
<td>Cyclopentane</td>
<td>259.4</td>
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<td>Methyl cyclopentane</td>
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<td>-1.05</td>
</tr>
<tr>
<td>Ethyl cyclopentane</td>
<td>374.7</td>
<td>-1.91</td>
</tr>
<tr>
<td>n-Propyl cyclopentane</td>
<td>417.4</td>
<td>2.34</td>
</tr>
<tr>
<td>n-Butyl cyclopentane</td>
<td>467.1</td>
<td>3.44</td>
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<td></td>
<td>$V_c$ c.c./g. mole</td>
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<tr>
<td></td>
<td>Exptl.</td>
<td>Calcd.</td>
</tr>
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<td>5. Cyclohexanes</td>
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<td>n-Propyl cyclohexane</td>
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<td>n-Butyl cyclohexane</td>
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<td>221.4</td>
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<td>Iso-propyl alcohol</td>
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<td>277.4</td>
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<tr>
<td>Iso-butyl alcohol</td>
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<td>501.4</td>
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<td>497.2</td>
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<td></td>
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<td>Methyl iso-propyl ketone</td>
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<td>Methyl iso-butyl ketone</td>
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<td>Average</td>
<td>211.0</td>
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</table>
A New Correlation to Predict Critical Volume

**TABLE 1—(contd.)**

Experimental and calculated values of critical volume.

<table>
<thead>
<tr>
<th></th>
<th>$V_c$ c.c./g. mole</th>
<th>% Error</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>8. Acids</strong></td>
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<tr>
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<td>Propionic acid</td>
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<td>227.6</td>
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<td>n-Butyric acid</td>
<td>290.0</td>
<td>283.6</td>
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<tr>
<td>Iso-butyric acid</td>
<td>292.0</td>
<td>279.4</td>
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<td>n-Valeric acid</td>
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<td>339.6</td>
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<td>335.4</td>
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<tr>
<td><strong>Average</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| **9. Ethers**    |                    |         |
| Dimethyl ether   | 178.0              | 165.1   | -9.95$^e$|
| Ethyl methyl ether | 221.0           | 221.1   | 0.05    |
| Diethyl ether    | 274.0              | 277.1   | 1.13    |
| Ethyl propyl ether | 339.0           | 333.1   | -1.73   |
| Iso-propyl ether | 382.0$^d$          | 384.9   | 0.76    |
| Vinyl ethyl ether | 260.0$^d$         | 260.4   | 0.17    |
| **Average**      |                    |         | 0.76    |

| **10. Esters**   |                    |         |
| Methyl formate   | 172.0              | 170.7   | -0.76   |
| Ethyl formate    | 229.0              | 226.6   | -1.05   |
| Propyl formate   | 225.0              | 283.0   | -0.93   |
| Amyl formate     | 381.0$^d$          | 395.0   | 3.68    |
| Iso-amyl formate | 391.0$^d$          | 390.0   | -0.33   |
| Methyl acetate   | 228.0              | 226.6   | -0.62   |
| Ethyl acetate    | 286.0              | 283.0   | -1.05   |
| n-Propyl acetate | 345.0              | 339.0   | -1.80   |
| n-Butyl acetate  | 395.0              | 395.0   | 0.00    |
| Iso-amyl acetate | 446.0$^d$          | 446.5   | 0.11    |
| Methyl propionate | 282.0            | 283.0   | 0.36    |
| Ethyl propionate | 345.0              | 338.8   | -1.80   |
Table 1—(contd.)
Experimental and calculated values of critical volume.

<table>
<thead>
<tr>
<th></th>
<th>( V_c ) c.c./g. mole</th>
<th>Calcd.</th>
<th>% Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propyl propionate</td>
<td>395.0&lt;sup&gt;d&lt;/sup&gt;</td>
<td>395.0</td>
<td>0.00</td>
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<tr>
<td>Iso-butyl propionate</td>
<td>446.0&lt;sup&gt;d&lt;/sup&gt;</td>
<td>446.5</td>
<td>0.11</td>
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<td>Iso-amyl propionate</td>
<td>501.0&lt;sup&gt;d&lt;/sup&gt;</td>
<td>502.0</td>
<td>0.20</td>
</tr>
<tr>
<td>Methyl butyrate</td>
<td>340.0</td>
<td>338.6</td>
<td>-0.35</td>
</tr>
<tr>
<td>n-Propyl butyrate</td>
<td>450.0&lt;sup&gt;d&lt;/sup&gt;</td>
<td>450.5</td>
<td>0.11</td>
</tr>
<tr>
<td>Iso-butyl butyrate</td>
<td>501.0&lt;sup&gt;d&lt;/sup&gt;</td>
<td>502.0</td>
<td>0.20</td>
</tr>
<tr>
<td>Iso-amyl n-butyrate</td>
<td>556.0&lt;sup&gt;d&lt;/sup&gt;</td>
<td>558.0</td>
<td>0.36</td>
</tr>
<tr>
<td>Methyl iso-butyrate</td>
<td>339.0</td>
<td>334.0</td>
<td>-1.48</td>
</tr>
<tr>
<td>n-Propyl iso-butyrate</td>
<td>446.0&lt;sup&gt;d&lt;/sup&gt;</td>
<td>446.5</td>
<td>0.11</td>
</tr>
<tr>
<td>Iso-butyl iso-butyrate</td>
<td>497.0&lt;sup&gt;d&lt;/sup&gt;</td>
<td>498.0</td>
<td>0.21</td>
</tr>
<tr>
<td>Ethyl iso-valerate</td>
<td>446.0&lt;sup&gt;d&lt;/sup&gt;</td>
<td>446.5</td>
<td>0.11</td>
</tr>
<tr>
<td>n-Propyl iso-valerate</td>
<td>501.0&lt;sup&gt;d&lt;/sup&gt;</td>
<td>502.0</td>
<td>0.20</td>
</tr>
<tr>
<td>Iso-butyl iso-valerate</td>
<td>552.0&lt;sup&gt;d&lt;/sup&gt;</td>
<td>555.0</td>
<td>0.55</td>
</tr>
<tr>
<td>Ethyl n-caprylate</td>
<td>615.0&lt;sup&gt;d&lt;/sup&gt;</td>
<td>618.0</td>
<td>0.49</td>
</tr>
</tbody>
</table>

Average 0.65

11. Halogenated Hydrocarbons

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl chloride</td>
<td>143.0</td>
<td>144.9</td>
<td>1.38</td>
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<tr>
<td>Methyl bromide</td>
<td>165.0&lt;sup&gt;d&lt;/sup&gt;</td>
<td>162.9</td>
<td>-1.27</td>
</tr>
<tr>
<td>Methyl iodide</td>
<td>190.0&lt;sup&gt;d&lt;/sup&gt;</td>
<td>194.1</td>
<td>2.16</td>
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<tr>
<td>Methylene Chloride</td>
<td>193.0&lt;sup&gt;d&lt;/sup&gt;</td>
<td>200.5</td>
<td>3.97</td>
</tr>
<tr>
<td>Fluoroform</td>
<td>145.0&lt;sup&gt;d&lt;/sup&gt;</td>
<td>147.9</td>
<td>2.01</td>
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<tr>
<td>Carbon tetrafluoride</td>
<td>153.0&lt;sup&gt;d&lt;/sup&gt;</td>
<td>148.7</td>
<td>2.80</td>
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<tr>
<td>Ethyl fluoride</td>
<td>168.0&lt;sup&gt;d&lt;/sup&gt;</td>
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<td>4.61</td>
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<tr>
<td>Ethyl chloride</td>
<td>199.0</td>
<td>200.9</td>
<td>0.95</td>
</tr>
<tr>
<td>Ethyl bromide</td>
<td>215.0</td>
<td>218.9</td>
<td>1.81</td>
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<tr>
<td>Propyl chloride</td>
<td>254.0</td>
<td>256.9</td>
<td>1.17</td>
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<tr>
<td>Dibromo ethane</td>
<td>235.0</td>
<td>236.4</td>
<td>0.59</td>
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<tr>
<td>1,1-Dichloro ethane</td>
<td>244.0&lt;sup&gt;d&lt;/sup&gt;</td>
<td>256.6</td>
<td>5.14</td>
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<tr>
<td>Allyl chloride</td>
<td>234.0&lt;sup&gt;d&lt;/sup&gt;</td>
<td>240.3</td>
<td>2.70</td>
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<tr>
<td>Bromo-trifluoromethane</td>
<td>205.0&lt;sup&gt;d&lt;/sup&gt;</td>
<td>207.4</td>
<td>1.18</td>
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<tr>
<td>Dichloro-difluoromethane</td>
<td>218.0</td>
<td>230.2</td>
<td>5.61</td>
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</table>

Average 2.42
### A New Correlation to Predict Critical Volume

**Table 1 (contd.)**

Experimental and calculated values of critical volume.

<table>
<thead>
<tr>
<th></th>
<th>( V_c ) c.c./g. mole</th>
<th>% Error</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Exptl.</td>
<td>Calcd.</td>
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<tr>
<td><strong>12. Halobenzenes</strong></td>
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<td></td>
</tr>
<tr>
<td>Chlorebenzene</td>
<td>308.0</td>
<td>307.6</td>
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<tr>
<td>Bromobenzene</td>
<td>324.0</td>
<td>325.5</td>
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<tr>
<td>Fluorobenzene</td>
<td>271.0</td>
<td>266.8</td>
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<tr>
<td>Iodobenzene</td>
<td>351.0</td>
<td>357.8</td>
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<tr>
<td>Dichlorobenzene</td>
<td>360.0</td>
<td>363.2</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>13. Aromatics</strong></td>
<td></td>
<td></td>
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<tr>
<td>Benzene</td>
<td>260.3</td>
<td>257.1</td>
</tr>
<tr>
<td>Toluene</td>
<td>319.9(^c)</td>
<td>313.1</td>
</tr>
<tr>
<td>Ethyl benzene</td>
<td>366.0</td>
<td>369.1</td>
</tr>
<tr>
<td>n-Propyl benzene</td>
<td>439.8</td>
<td>425.1</td>
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<tr>
<td>n-Butyl benzene</td>
<td>498.0</td>
<td>481.1</td>
</tr>
<tr>
<td>n-Pentyl benzene</td>
<td>521.5(^c)</td>
<td>537.1</td>
</tr>
<tr>
<td>n-Hexyl benzene</td>
<td>582.5(^c)</td>
<td>593.1</td>
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<tr>
<td>n-Heptyl benzene</td>
<td>642.9(^e)</td>
<td>649.1</td>
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<tr>
<td>n-Octyl benzene</td>
<td>702.0(^e)</td>
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<td>n-Nonyl benzene</td>
<td>759.4(^e)</td>
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<tr>
<td>n-Undecyl benzene</td>
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<td>878.0</td>
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<tr>
<td>n-Dodecyl benzene</td>
<td>935.8(^e)</td>
<td>935.4</td>
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<tr>
<td>n-Tridecyl benzene</td>
<td>994.9(^e)</td>
<td>991.8</td>
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<tr>
<td>n-Tetradecyl benzene</td>
<td>1052.4(^e)</td>
<td>1048.2</td>
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<tr>
<td>n-Pentadecyl benzene</td>
<td>1109.6(^e)</td>
<td>1104.7</td>
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<tr>
<td>n-Hexadecyl benzene</td>
<td>1168.0(^e)</td>
<td>1161.1</td>
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<tr>
<td><strong>Average</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>14. Sulphur Compounds</strong></td>
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</tr>
<tr>
<td>Methyl mercaptan</td>
<td>149.0</td>
<td>148.1</td>
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<tr>
<td>Ethyl mercaptan</td>
<td>207.0</td>
<td>204.1</td>
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<tr>
<td>Dimethyl sulfide</td>
<td>201.0</td>
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<td>Methyl ethyl sulfide</td>
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<td>Diethyl sulfide</td>
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<tr>
<td>Diethyl disulfide</td>
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<td>Allyl sulfide</td>
<td>385.0(^d)</td>
<td>394.8</td>
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<tr>
<td><strong>Average</strong></td>
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</tbody>
</table>

\[
% \text{ Error} = \left( \frac{\text{Exptl.} - \text{Calcd.}}{\text{Exptl.}} \right) \times 100
\]

\(^c\) - Dreisbach (2)

\(^d\) - Lydersen's (4)

* - Values not used to find average errors.
TABLE 2
Group contribution to evaluate constants in Equation 9

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<thead>
<tr>
<th>Atomic contribution to evaluate C</th>
<th>Group contribution to evaluate C</th>
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<tr>
<td>CH(_2) in (CH(_2))(_n)</td>
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<tr>
<td>n \leq 12</td>
<td>56.00</td>
</tr>
<tr>
<td>n &gt; 12</td>
<td>56.42</td>
</tr>
<tr>
<td>C</td>
<td>12.60</td>
</tr>
<tr>
<td>H</td>
<td>21.70</td>
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<tr>
<td>H in OH</td>
<td>14.00</td>
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<tr>
<td>O</td>
<td>27.72</td>
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<tr>
<td>O(_2) in esters</td>
<td>76.12</td>
</tr>
<tr>
<td>N</td>
<td>24.50</td>
</tr>
<tr>
<td>S</td>
<td>68.74</td>
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<td>P</td>
<td>56.70</td>
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<td>F</td>
<td>36.54</td>
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<td>Cl</td>
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<td>Br</td>
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<tr>
<td>I</td>
<td>126.42</td>
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<tr>
<td>Double bond</td>
<td>26.74</td>
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<tr>
<td>Triple bond</td>
<td>56.84</td>
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<tr>
<td>Carbonyl bond in Ketones:</td>
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</tr>
<tr>
<td>Total number of Carbon atoms:</td>
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<td>3</td>
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<td>4</td>
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<td>7</td>
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<td>8</td>
<td>21.14</td>
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<td>9</td>
<td>19.74</td>
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<tr>
<td>10</td>
<td>18.20</td>
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<tr>
<td>Ring closure:</td>
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<td>17.50</td>
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<tr>
<td>4 membered ring</td>
<td>8.40</td>
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<tr>
<td>5 membered ring</td>
<td>4.20</td>
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<tr>
<td>6 membered ring</td>
<td>1.12</td>
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<td>7 membered ring</td>
<td>5.60</td>
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<tr>
<td>Chain branching</td>
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<tr>
<td>per branch</td>
<td>-4.2</td>
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</tbody>
</table>

Base group CH\(_3\)  
Addition or subtraction of H  
Double bond  
Triple bond  
OH group in alcohols  
CO group in ketones  
COOH group in acids  
O in ethers  
COO group in esters  
Halogen addition replacing H in aliphatic compounds  
Halogen addition replacing H in aromatic compounds  
Aromatic ring closure  
Aliphatic ring closure (5 membered)  
Aliphatic ring closure (6 membered)
<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Series</th>
<th>Number considered</th>
<th>Constant C</th>
<th>% average error</th>
<th>% Average Error in $Y$, calculated by the method due to...</th>
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<tr>
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<td>Authors</td>
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<tr>
<td>1.</td>
<td>Paraffins</td>
<td>34</td>
<td>$-8$</td>
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<td>Mono-olefins</td>
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<td>$-5$</td>
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<td>$-15$</td>
<td>0.69</td>
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<tr>
<td>4.</td>
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<td>$-25$</td>
<td>1.60</td>
<td>3</td>
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<tr>
<td>5.</td>
<td>Cyclohexanes</td>
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<td>1.01</td>
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<td>8.</td>
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<td>1.36</td>
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<tr>
<td>9.</td>
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<td>0.76</td>
<td>4</td>
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<td>10.</td>
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<td>26</td>
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<td>0.65</td>
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<td>Halogenated hydrocarbons</td>
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<td>159</td>
<td>Av Abs. deviation</td>
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<td></td>
<td>1.31</td>
<td>83</td>
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</tbody>
</table>

The number in bracket indicates the number of compounds considered if different from present comparison.
NOMENCLATURE

\( A \) = Constant in Equation [9].
\( h_0 \) = Hard sphere volume, c.c./g. mole.
\( C \) = Constant in Equation [1].
\( [P] \) = Parachor.
\( V_c \) = Critical volume, c.c./g. mole.
\( \sigma \) = Intermolecular distance, Å.
\( \epsilon \) = Minimum potential energy, ergs.

REFERENCES


