Example 7-10: Estimation of critical temperature and critical pressure using the Joback method.

The chemical compound of interest is: CH$_3$-CHCl-CH$_2$-CHCl-CH$_2$-CH=CH$_2$

Estimate the critical temperature and critical pressure of this compound using group additivity.

*Step 1 - Identify the groups within the compound.*

The complete list of groups identified within the Joback method is in Appendix G. In this case, the compound contains:

One –CH$_3$ group

Two –CH$_2$– groups

Two >CH- groups

Two –Cl groups

One =CH- group

One =CH$_2$ group

**Pitfall Prevention:** One likely error is confusing the “CH$_2$” groups. There are three C atoms that are each bonded to two H atoms, and in that sense there are three “CH$_2$” groups. But these “groups” are distinguished from each other by how the other two bond positions on the C are filled: one “CH$_3$” carbon has a double-bond (=CH$_2$), the others have two single bonds (–CH$_2$–).
Step 2- Identify relevant equations

From Appendix G, the Joback equations for critical temperature and critical pressure are:

\[
T_c = T_b \left[ 0.584 + 0.965 \Sigma - (\Sigma)^2 \right]^{-1}
\]  
(7.84)

\[
P_c = (0.113 + 0.0032n_a - \Sigma)^{-2}
\]  
(7.85)

Where \( n_a \) is the number of atoms and \( \Sigma \) represents the sum of the contributions of individual groups to the property. The formula for \( T_c \) requires the normal boiling point \( T_b \). We would use an experimental value of \( T_b \) if we had one, but as it is, we will estimate this too from the Joback method:

\[
T_b = 198.2 + \Sigma
\]  
(7.86)

Step 3- Sum group contributions

The contribution of each group to each property is obtained from Appendix G. The results are summarized in Error! Reference source not found.
### Table 7-9: Applying the Joback group additivity method to the compound CH$_3$-CHCl-CH$_2$-CHCl-CH$_2$-CH=CH$_2$

<table>
<thead>
<tr>
<th>Group</th>
<th># occurrences</th>
<th>$T_b$</th>
<th>$T_c$</th>
<th>$P_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>−CH$_3$</td>
<td>1</td>
<td>23.58</td>
<td>0.0141</td>
<td>-0.0012</td>
</tr>
<tr>
<td>−CH$_2$−</td>
<td>2</td>
<td>2 × 22.88</td>
<td>2 × 0.0189</td>
<td>2 × 0</td>
</tr>
<tr>
<td>&gt;CH−</td>
<td>2</td>
<td>2 × 21.74</td>
<td>2 × 0.0164</td>
<td>2 × 0.0020</td>
</tr>
<tr>
<td>−Cl</td>
<td>2</td>
<td>2 × 38.13</td>
<td>2 × 0.0105</td>
<td>2 × (-0.0049)</td>
</tr>
<tr>
<td>=CH−</td>
<td>1</td>
<td>24.96</td>
<td>0.0129</td>
<td>-0.0006</td>
</tr>
<tr>
<td>=CH$_2$</td>
<td>1</td>
<td>18.18</td>
<td>0.0113</td>
<td>-0.0028</td>
</tr>
<tr>
<td>Σ</td>
<td></td>
<td>232.22</td>
<td>0.1299</td>
<td>-0.0104</td>
</tr>
</tbody>
</table>

**Step 4: Compute properties**

Substituting the results from Error! Reference source not found. into equations 7.71-7.73 gives,

for normal boiling point:

$$T_b = 198.2 + \Sigma = 198.2 + 232.22 = 430.42 \text{ K} \quad (7.87)$$

For critical temperature:

$$T_c = T_b[0.584 + 0.965\Sigma - (\Sigma)^2]^{-1} \quad (7.88)$$

$$T_c = (430.42 \text{ K})[0.584 + 0.965(0.1299) - (0.1299)^2]^{-1} = 621.6 \text{ K}$$
For critical pressure, the number of atoms is \( n_a = 21 \) (7 C, 12 H, 2 Cl) and the estimated \( P_c \) is:

\[
P_c = (0.113 + 0.0032n_a - \Sigma)^{-2}
\]

\[
P_c = [0.113 + 0.0032(21) - (-0.0104)]^{-2} = 27.53 \text{ bar}
\]

Step 5 - Assessing accuracy

This compound is a di-chloro-heptene. It is not a prominent enough chemical product to appear in mainstream resources like the NIST Webbook, the CRC Handbook of Chemistry and Physics or Perry’s Chemical Engineers Handbook. The value of group additivity schemes is they allow us to generate an estimate of physical properties when no data is available. But how accurate is the estimate? One way to benchmark this is to apply the Joback method to the compound 1-heptene, the most similar compound for which data is readily available.

The compound 1-heptene:

\[
\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}=\text{CH}_2
\]

Is comprised of the following groups:

One \(-\text{CH}_3\) group

Four \(-\text{CH}_2\) groups

One \(-\text{CH}\) group

One \(-\text{CH}_2\) group
Table 7-9a: Applying the Joback group additivity method to the compound 1-heptene

<table>
<thead>
<tr>
<th>Group</th>
<th># occurrences</th>
<th>( T_b )</th>
<th>( T_c )</th>
<th>( P_c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>–CH(_3)</td>
<td>1</td>
<td>23.58</td>
<td>0.0141</td>
<td>-0.0012</td>
</tr>
<tr>
<td>–CH(_2)</td>
<td>4</td>
<td>4 × 22.88</td>
<td>4 × 0.0189</td>
<td>4 × 0</td>
</tr>
<tr>
<td>=CH(_-)</td>
<td>1</td>
<td>24.96</td>
<td>0.0129</td>
<td>-0.0006</td>
</tr>
<tr>
<td>=CH(_2)</td>
<td>1</td>
<td>18.18</td>
<td>0.0113</td>
<td>-0.0028</td>
</tr>
<tr>
<td>Σ</td>
<td></td>
<td>158.24</td>
<td>0.1139</td>
<td>-0.0046</td>
</tr>
</tbody>
</table>

Substituting the results from Error! Reference source not found.a into equations 7.71-7.73 gives,

for normal boiling point:

\[
T_b = 198.2 + \Sigma = 198.2 + 158.24 = 356.44 \text{ K}
\]

For critical temperature:

\[
T_c = T_b [0.584 + 0.965\Sigma - (\Sigma)^2]^{-1}
\]

\[
T_c = (356.44 \text{ K}) [0.584 + 0.965(0.1139) - (0.1139)^2]^{-1} = 523.5 \text{ K}
\]

For critical pressure, the number of atoms is \( n_a = 21 \) (7 C, 14 H) and the estimated \( P_c \) is:

\[
P_c = (0.113 + 0.0032n_a - \Sigma)^{-2}
\]

\[
P_c = [0.113 + 0.0032(21) - (-0.0046)]^{-2} = 29.3 \text{ bar}
\]
The experimental values, according to *The Properties of Gases and Liquids* (Poling, 2001), are \( T_c = 537.3 \) and \( P_c = 29.2 \) bar. Consequently the predictions from the Joback method are accurate within \(~2.5\%\) for the temperature and \(~0.5\%\) for the pressure.