MKS-03409: Effect of Pressure on the Melting Point
by Dr. Kevin G. Joback
May 11, 2005

Abstract
A chemical’s melting point is typically assumed to be independent of pressure. However, as more processes begin operating at high pressure, it is important to understand just how pressure affects the melting point and how this effect can be estimated.

Effect of Pressure
Figure 1 shows the melting point as a function of pressure for methanol [1], ethanol [1], and acetone [2]. The curves show melting point increases with an increase in pressure. Although there are some common exceptions, e.g., water, this trend is true for the majority of compounds.

Table 1 compares melting points at atmospheric pressure with those at 98.7 atm (10 MPa) for these three chemicals. The numerical values show that the general assumption of pressure independence is quite valid.
Table 1: Evaluation of Pressure Independence Assumption

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Tm [K] @ 1 atm</th>
<th>Tm [K] @ 98.7 atm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>175.47</td>
<td>176.61</td>
</tr>
<tr>
<td>Ethanol</td>
<td>159.05</td>
<td>159.79</td>
</tr>
<tr>
<td>Acetone</td>
<td>176.35</td>
<td>179.95</td>
</tr>
</tbody>
</table>

Estimating the Effect of Pressure

The Clapeyron equation, shown in Equation 1, describes the effect of pressure on the equilibrium melting point.

\[
\frac{dT_m}{dP} = \frac{T_m \Delta V_m}{\Delta H_{fus}}
\]

In Equation 1 \(T_m\) is the equilibrium melting point, \(P\) is the pressure, \(\Delta V_m\) is equal to the liquid molar volume minus the solid molar volume, and \(\Delta H_{fus}\) is the enthalpy of fusion.

Integrating Equation 1 requires knowing the liquid volume, solid volume, and the enthalpy of fusion as functions of pressure. Such relationships are seldom available. One possible approach is to assume these properties are independent of pressure. Equation 2 shows the result of using this assumption and using the melting point at atmospheric pressure as a boundary condition to integrate Equation 1.

\[
\ln T_m - \ln T_{m,1\text{ atm}} = \frac{\Delta V_m}{\Delta H_{fus}} (P - 101325)
\]

Here \(T_{m,1\text{ atm}}\) is the chemical’s melting point at 1 atmosphere pressure and \(P\) is the pressure in units of Pa.

Table 2 shows values for solid molar volume, liquid molar volume, and enthalpy of fusion all measured at temperatures near the atmospheric melting temperature [3].

Table 2: Properties Needed for Equation 2

<table>
<thead>
<tr>
<th>Chemical</th>
<th>(V_s) [m3/kmol]</th>
<th>(V_l) [m3/kmol]</th>
<th>(\Delta H_{fus}) [J/kmol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>0.03270</td>
<td>0.03616</td>
<td>3.2049E6</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.04367</td>
<td>0.05115</td>
<td>4.9310E6</td>
</tr>
<tr>
<td>Acetone</td>
<td>0.05996</td>
<td>0.06361</td>
<td>5.6912E6</td>
</tr>
</tbody>
</table>
Figure 2 compares estimates from Equation 2 with data for methanol. Similar results for ethanol and acetone indicate that the “pressure independent” assumption does not produce good results.

![Figure 2: “Pressure Independent” Clapeyron Equation Estimates and Data for Methanol](image)

### The Simon Equation

Equation 3 shows the relationship proposed by Simon and Glatzel [4].

\[
\frac{P - P_{tp}}{a} = \left( \frac{T_m}{T_{m,1atm}} \right)^b - 1
\]

In Equation 3, P is the pressure, \(P_{tp}\) is the triple point pressure, \(T_m\) is the equilibrium melting point at pressure P, \(T_{m,1atm}\) is the melting point at 1 atmosphere pressure, and a and b are regression constants. \(P_{tp}\) can often be neglected because it is much smaller than P in value.

Babb [5] compiled parameters for the Simon equation for over 200 chemicals. Table 3 lists parameters for several of these chemicals. These parameters, accompanying data, and additional parameters regressed from data, have been added to various Molecular Knowledge Systems® [6] knowledge bases and can be accessed by Cranium® [6] version 2 and later.
Table 3: Parameters for the Simon Equation for Several Chemicals

<table>
<thead>
<tr>
<th>Chemical</th>
<th>a [MPa]</th>
<th>b [- - -]</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>412.2</td>
<td>2.937</td>
<td>Note 1</td>
</tr>
<tr>
<td>Ethanol</td>
<td>931.1</td>
<td>1.398</td>
<td>Note 1</td>
</tr>
<tr>
<td>Acetone</td>
<td>119.7</td>
<td>4.137</td>
<td>Note 2</td>
</tr>
<tr>
<td>n-Octadecane</td>
<td>345</td>
<td>3.39</td>
<td>Ref 5</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>525</td>
<td>2.06</td>
<td>Ref 5</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>760</td>
<td>2.20</td>
<td>Ref 5</td>
</tr>
</tbody>
</table>

Note 1: Regressed from the data of reference 1. Note 2: Regressed from the data of reference 2.

Figure 3 compares the parameter fits to the experimental data for methanol, ethanol, and acetone. A legend is not shown on the graph but the symbols and colors are the same as those used in Figure 1. The Simon equation reproduces the data very well.

Figure 3: Comparison of the Simon Equation Estimates to Experimental Data. (See Figure 1 for graph’s legend.)

Conclusion
The Simon equation fits experimental data very well. Caution must be taken to ensure solid-solid transitions do not occur over the range of values being regressed. Care must also be taken when using published parameters. For example, the published parameters for ethanol [5] fit the experimental data [1] very poorly. Molecular Knowledge Systems, Inc. is reexamining these published parameter values. We are also investigating how to predict parameters from knowledge of only the chemical’s molecular structure.
References
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