Example Using the Clausius-Clapeyron Equation
Dexter Perkins

Consider the reaction between grossular, corundum, anorthite and gehlenite:
\[ \text{Gr} + \text{Co} = \text{An} + \text{Ge} \]

Boettcher (1970) determined that this reaction takes place between 760 and 780 °C at 1 Kbar pressure.

Use Boettcher's results as a starting point and apply the Clausius-Clapeyron Equation to determine the temperature of reaction at 10 Kbar.

To do this:

This is a solid-solid reaction, so it is reasonable to assume that \( \Delta S / \Delta V \) of reaction is about constant. So we can calculate the slope of the reaction at 1bar and use that to extrapolate.

From thermodynamic reference books, we find the following 1-bar molar entropy and volume values for the four phases involved:

<table>
<thead>
<tr>
<th>Phase</th>
<th>( S ) (J/deg mol)</th>
<th>( V ) (Cm(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gr</td>
<td>255.5</td>
<td>125.3</td>
</tr>
<tr>
<td>Co</td>
<td>50.92</td>
<td>25.575</td>
</tr>
<tr>
<td>An</td>
<td>199.3</td>
<td>100.79</td>
</tr>
<tr>
<td>Ge</td>
<td>209.8</td>
<td>90.24</td>
</tr>
</tbody>
</table>

From these values we can calculate the \( \Delta V \) and \( \Delta S \) of reaction:

\[
\Delta V = V_{\text{An}} + V_{\text{Ge}} - V_{\text{Gr}} - V_{\text{Co}} = 100.79 + 90.24 - 125.3 - 25.575 = 40.155 \text{ Cm}^3/\text{mol}
\]

\[
\Delta S = S_{\text{An}} + S_{\text{Ge}} - S_{\text{Gr}} - S_{\text{Co}} = 199.3 + 209.8 - 255.5 - 50.92 = 102.68 \text{ J/deg} \cdot \text{mol}
\]

We need a conversion factor to help with the units:

10 Cm\(^3\) = 1 J/bar

So, \( \Delta V = 4.0155 \) J/mol

The Clausius-Clapeyron equations says that:

\[
dP/dT = \Delta S / \Delta V = 102.68/4.0155 = 25.57 \text{ bar/deg}
\]

Using this value, we find that if the reaction takes place at 770 °C at 1 Kbar, it must take place at 1121 °C at 10 Kbar.

Figure 1. The reaction Gr+Co=An+Ge extracted from Boettcher's (1970) experimental results (solid and open circles) to 10 Kbar.