The value of \( (K_{p1}) \) is independent of pressure, although the composition of a system at equilibrium may be very much dependent on pressure. Temperature dependence is another matter. Because the value of \( \Delta G_{rxm}^o \) is dependent on temperature, the value of \( (K_{p1}) \) is as well. The form of the temperature dependence can be taken from the definition of the Gibbs function. At constant temperature and pressure

\[
\dfrac{\Delta G^o_{T_2}}{T_2} - \dfrac{\Delta G^o_{T_1}}{T_1} = \Delta H^o \left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right)
\]

Substituting

\[
\Delta G^o = -RT \ln K
\]

For the two values of \( \Delta G^o \) and using the appropriate temperatures, yields

\[
\dfrac{-R{T_2} \ln K_2}{T_2} - \dfrac{-R{T_1} \ln K_1}{T_1} = \Delta H^o \left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right)
\]

And simplifying the expression so that only terms involving \( (K) \) are on the left and all other terms are on the right results in the van’t Hoff equation, which describes the temperature dependence of the equilibrium constant.

\[
\ln \left(\dfrac{K_2}{K_1}\right) = - \dfrac{\Delta H^o}{R} \left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right)
\]

Because of the assumptions made in the derivation of the Gibbs-Helmholtz equation, this relationship only holds if \( \Delta H^o \) is independent of temperature over the range being considered. This expression also suggests that a plot of \( \ln(K) \) as a function of \( 1/T \) should produce a straight line with a slope equal to \( -\Delta H^o / R \). Such a plot is known as a van’t Hoff plot, and can be used to determine the reaction enthalpy.

Example \( \PageIndex{1} \)

A certain reaction has a value of \( (K_{p1} = 0.0260) \) at 25 °C and \( \Delta H_{rxm}^o = 32.4 \text{kJ/mol} \). Calculate the value of \( (K_{p2}) \) at 37 °C.

Solution

This is a job for the van’t Hoff equation!

- \( T_1 = 298 \text{ K} \)
- \( T_2 = 310 \text{ K} \)
- \( \Delta H_{rxm}^o = 32.4 \text{ kJ/mol} \)
- \( K_1 = 0.0260 \)
- \( K_2 = ? \)

So Equation \ref{vH} becomes

\[
\begin{align*}
\ln \left(\dfrac{K_2}{0.0260}\right) &= - \dfrac{32400 \text{ J/mol}}{8.314 \text{ K/mol K}} \left(\dfrac{1}{310 \text{ K}} - \dfrac{1}{298 \text{ K}}\right) \\
K_2 &= 0.0431
\end{align*}
\]

Note: the value of \( (K_{2}) \) increased with increasing temperature, which is what is expected for an endothermic reaction.
reaction. An increase in temperature should result in an increase of product formation in the equilibrium mixture. But unlike a change in pressure, a change in temperature actually leads to a change in the value of the equilibrium constant!

Example \(\PageIndex{2}\)

Given the following average bond enthalpies for \(\ce{P-Cl}\) and \(\ce{Cl-Cl}\) bonds, predict whether or not an increase in temperature will lead to a larger or smaller degree of dissociation for the reaction

\[
\ce{PCl_5 \rightleftharpoons PCl_3 + Cl_2}
\]

<table>
<thead>
<tr>
<th>X-Y</th>
<th>D(X-Y) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-Cl</td>
<td>326</td>
</tr>
<tr>
<td>Cl-Cl</td>
<td>240</td>
</tr>
</tbody>
</table>

**Solution**

The estimated reaction enthalpy is given by the total energy expended breaking bonds minus the energy recovered by the formation of bonds. Since this reaction involves breaking two P-Cl bonds (costing 652 kJ/mol) and the formation of one Cl-Cl bond (recovering 240 kJ/mol), it is clear that the reaction is endothermic (by approximately 412 kJ/mol). As such, an increase in temperature should increase the value of the equilibrium constant, causing the degree of dissociation to be increased at the higher temperature.