It is often required to know thermodynamic functions (such as enthalpy) at temperatures other than those available from tabulated data. Fortunately, the conversion to other temperatures is not difficult.

At constant pressure

\[ dH = C_p \,dT \]

And so for a temperature change from \( T_1 \) to \( T_2 \)

\[ \Delta H = \int_{T_1}^{T_1} C_p \,dT \]

Equation \ref{EQ1} is often referred to as Kirchhoff's Law. If \( C_p \) is independent of temperature, then

\[ \Delta H = C_p \,\Delta T \]

If the temperature dependence of the heat capacity is known, it can be incorporated into the integral in Equation \ref{EQ1}. A common empirical model used to fit heat capacities over broad temperature ranges is

\[ C_p(T) = a + bT + \frac{c}{T^2} \]

After combining Equations \ref{EQ15} and \ref{EQ1}, the enthalpy change for the temperature change can be found obtained by a simple integration

\[ \Delta H = \int_{T_1}^{T_2} \left(a + bT + \frac{c}{T^2}\right) dT \]

Solving the definite integral yields

\[
\begin{align}
\Delta H &= a(T_2 - T_1) + b\left(\frac{T_2^2 - T_1^2}{2}\right) + c\left(\frac{1}{T_2} - \frac{1}{T_1}\right)
\end{align}
\]

This expression can then be used with experimentally determined values of \( a \), \( b \), and \( c \), some of which are shown in the following table.

<table>
<thead>
<tr>
<th>Substance</th>
<th>( a ) (J mol(^{-1}) K(^{-1}))</th>
<th>( b ) (J mol(^{-1}) K(^{-2}))</th>
<th>( c ) (J mol(^{-1}) K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(gr)</td>
<td>16.86</td>
<td>4.77 \times 10^{-3}</td>
<td>-8.54 \times 10^5</td>
</tr>
<tr>
<td>CO(_2)(g)</td>
<td>44.22</td>
<td>8.79 \times 10^{-3}</td>
<td>-8.62 \times 10^5</td>
</tr>
<tr>
<td>H(_2)O(l)</td>
<td>75.29</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>N(_2)(g)</td>
<td>28.58</td>
<td>3.77 \times 10^{-3}</td>
<td>-5.0 \times 10^4</td>
</tr>
<tr>
<td>Pb(s)</td>
<td>22.13</td>
<td>1.172 \times 10^{-2}</td>
<td>9.6 \times 10^4</td>
</tr>
</tbody>
</table>
Example 1: Heating Lead

What is the molar enthalpy change for a temperature increase from 273 K to 353 K for Pb(s)?

Solution:

The enthalpy change is given by Equation 1 with a temperature dependence \(C_p\) given by Equation 1 using the parameters in Table 1. This results in the integral form (Equation 2):

\[
\Delta H = a(T_2-T_1) + \dfrac{b}{2}(T_2^2-T_1^2) - c \left( \dfrac{1}{T_2} - \dfrac{1}{T_1} \right)
\]

when substituted with the relevant parameters of Pb(s) from Table 1.

\[
\begin{align*}
\Delta H = & \left(22.14 \dfrac{J}{mol\,K} (353\,K - 273\,K) \right) + \dfrac{1.172 \times 10^{-2} \dfrac{J}{mol\,K^2}}{2} (353^2 - 273^2) - 9.6 \times 10^4 \dfrac{J\,K}{mol} \left( \dfrac{1}{353\,K} - \dfrac{1}{273\,K} \right) \nonumber \\Delta H = & \, 1770.4 \dfrac{J}{mol} + 295.5 \dfrac{J}{mol} + 470.5 \dfrac{J}{mol} \nonumber \Delta H = & \, 2534.4 \dfrac{J}{mol}
\end{align*}
\]

For chemical reactions, the reaction enthalpy at differing temperatures can be calculated from

\[
\Delta H_{rxn}(T_2) = \Delta H_{rxn}(T_1) + \int_{T_1}^{T_2} \Delta C_p \Delta T
\]

Example 2: Enthalpy of Formation

The enthalpy of formation of NH\(_3\) (g) is -46.11 kJ/mol at 25 °C. Calculate the enthalpy of formation at 100 °C.

Solution:

\[
\ce{N2(g) + 3 H2(g) \rightleftharpoons 2 NH3(g)} \nonumber
\]

with \(\Delta H \,(298\, K) = -46.11\, kJ/mol\)

<table>
<thead>
<tr>
<th>Compound</th>
<th>(C_p) (J mol(^{-1}) K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(_2)(g)</td>
<td>29.12</td>
</tr>
<tr>
<td>H(_2)(g)</td>
<td>28.82</td>
</tr>
<tr>
<td>NH(_3)(g)</td>
<td>35.06</td>
</tr>
</tbody>
</table>

\[
\begin{align*}
\Delta H (373\,K) \& = \Delta H (298\,K) + \Delta C_p \Delta T \nonumber \\
\Delta H (373\,K) \& = -46110 \dfrac{J}{mol} \left(35.06 \dfrac{J}{mol\,K} \right) - 9.6 \times 10^4 \dfrac{J\,K}{mol} \left( \dfrac{1}{353\,K} - \dfrac{1}{273\,K} \right) \nonumber \Delta H (373\,K) \& = -49.5 \dfrac{kJ}{mol}
\end{align*}
\]
Contributors

- Patrick E. Fleming (Department of Chemistry and Biochemistry; California State University, East Bay)