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 \(T_2\)

\[ \Delta H = \int_{T_2}^{T_2} C_p\,dT \tag{EQ1} \]

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

\[ \Delta H = C_p \Delta T \tag{intH} \]

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

\[ C_p(T) = a + bT + \frac{c}{T^2} \tag{EQ15} \]

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

\[ \Delta H = \int_{T_1}^{T_2} \left(a + bT + \frac{c}{T^2}\right)\,dT \tag{EQ2} \]

Solving the definite integral yields

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

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

\[ \text{Table } \PageIndex{1}: \text{ Empirical Parameters for the temperature dependence of } C_p \]

<table>
<thead>
<tr>
<th>Substance</th>
<th>(a ,(J \text{ mol}^{-1} \text{ K}^{-1}))</th>
<th>(b ,(J \text{ mol}^{-1} \text{ K}^{-2}))</th>
<th>(c ,(J \text{ mol}^{-1} \text{ K}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(gr)</td>
<td>16.86</td>
<td>4.77 x 10(^{-3})</td>
<td>-8.54 x 10(^5)</td>
</tr>
<tr>
<td>CO(_2)(g)</td>
<td>44.22</td>
<td>8.79 x 10(^{-3})</td>
<td>-8.62 x 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 x 10(^{-3})</td>
<td>-5.0 x 10(^4)</td>
</tr>
<tr>
<td>Pb(s)</td>
<td>22.13</td>
<td>1.172 x 10(^{-2})</td>
<td>9.6 x 10(^4)</td>
</tr>
</tbody>
</table>
Example \(\PageIndex{1}\): 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 \ref{EQ1} with a temperature dependence \(C_p\) given by Equation \ref{EQ1} using the parameters in Table \(\PageIndex{1}\). This results in the integral form (Equation \ref{ineq}):

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

when substituted with the relevant parameters of Pb(s) from Table \(\PageIndex{1}\)).

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

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

\[
\Delta H_{\text{rxn}}(T_\text{2}) = \Delta H_{\text{rxn}}(T_\text{1}) + \int_{T_\text{1}}^{T_\text{2}} \Delta C_p \Delta T
\]

**Example \(\PageIndex{2}\): Enthalpy of Formation**

The enthalpy of formation of \(\text{NH}_3\) (g) is -46.11 kJ/mol at 25 \(^\circ\)C. Calculate the enthalpy of formation at 100 \(^\circ\)C.

**Solution:**

\[
\begin{align*}
\Delta H (373, K) &= \Delta H (298, K) + \int_{298}^{373} \Delta C_p \Delta T \\
&= -46110 \dfrac{J}{mol} \left[2 \left(35.06 \dfrac{J}{mol \cdot K}\right) - \left(29.12 \dfrac{J}{mol \cdot K}\right) - 3 \left(28.82 \dfrac{J}{mol \cdot K}\right)\right] (373, K - 298, K) \\
&= -49.5 \dfrac{kJ}{mol}
\end{align*}
\]

\[
\begin{array}{|c|c|}
\hline
\text{Compound} & \text{Cp (J mol}^{-1} \text{K}^{-1}) \\
\hline
\text{N}_2\text{(g)} & 29.12 \\
\text{H}_2\text{(g)} & 28.82 \\
\text{NH}_3\text{(g)} & 35.06 \\
\hline
\end{array}
\]
Contributors

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