Previously, we introduced Serpentinization, the geothermal processes that heat water up to 91°C (196°F) in the geothermal vents in the Atlantic Massif[1]. A "Fly-in video" puts the formation into perspective.

The Atlantis Massif rises ~14,000 feet above the surrounding seafloor and is formed by long-lived faulting[2].

The actively venting 'IMAX' flange protrudes from the side of the massive Poseidon structure, photographed by the Hercules submersible[3].

Calculating the Heat Released by Serpentinization

By now chemists have measured the enthalpy changes for so many reactions that it would take several large volumes to list all the thermochemical equations. Now we'll see how the enthalpy of the serpentinization reaction, and many variations on it that might never get tabulated, can be easily calculated.

Metasomatic Talc-Serpentine
Schist Cut 3863-1419[4]

For example, if we’re interested in one of the main serpentinization reactions which provides heat to the thermal vents:

Forsterite + aqueous silica → serpentine (crysotile)

3 Mg$_2$SiO$_4$(s) + SiO$_2$(aq) + 4 H$_2$O(l) → 2 Mg$_3$Si$_2$O$_5$(OH)$_4$(s) (1)

We can use Hess’ law to calculate the $\Delta H_m$ from a single list of standard enthalpies of formation $\Delta H_f$, for all compounds. The standard enthalpy of formation is the enthalpy change when 1 mol of a pure substance is formed from its elements. Each element must be in the physical and chemical form which is most stable at normal atmospheric pressure and a specified temperature (usually 25°C).

For example, if we know that $\Delta H_f[H_2O(l)] = -285.8$ kJ mol$^{-1}$, we can immediately write the thermochemical equation

H$_2$(g) + ½O$_2$(g) → H$_2$O(l) $\Delta H_m = -285.8$ kJ mol$^{-1}$ (2) The elements H and O appear as diatomic molecules and in gaseous form because these are their most stable chemical and physical states. Note also that 285.8 kJ are given off per mole of H$_2$O(l) formed. Equation (1) must specify formation of 1 mol H$_2$O(l), and so the coefficient of O$_2$ must be $\frac{1}{2}$.

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**Example 1**

Calculate the Enthalpy change for Equation (1) from the heats of formation of the reactants and products.

<table>
<thead>
<tr>
<th></th>
<th>3 Mg$_2$SiO$_4$</th>
<th>+ SiO$_2$ (aq)</th>
<th>+ 4 H$_2$O</th>
<th>2 Mg$_3$Si$_2$O$_5$(OH)$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H_f$ kJ<em>mol$^{-1}^</em>$</td>
<td>-2173.6</td>
<td>-876.9</td>
<td>-285.8</td>
<td>-4360.3</td>
</tr>
</tbody>
</table>

*values from SUPCRT$^5$

**Solution** We can imagine that the reaction takes place in four steps, each of which involves only a standard enthalpy of formation. First, the reactants will be decomposed into their elements, then the elements will be recombined into the product.

In the first step H$_2$O(l) (water) is decomposed to its elements:

4H$_2$O(l) → 2 O$_2$(g) + 4H$_2$(g) $\Delta H_3$= (3)

Since this is the reverse of formation of 4 mol H$_2$O(l) from its elements, the enthalpy change is

$\Delta H_3 = 4$ mol × {−$\Delta H_f[H_2O(l)]$} = 4 mol × [- (−285.8 kJ mol$^{-1}$)] = +1143.2 kJ

In the second step the SiO$_2$(s) similarly decomposes into its elements, with an enthalpy change equal to the negative of its heat of formation:
SiO$_2$(s) → Si(s) + O$_2$(g) $\Delta H_4$ (4)

$\Delta H_4 = 1 \text{ mol} \times -\Delta H_f[\text{SiO}_2(g)] = 1 \text{ mol} \times -(–876.9 \text{ kJ mol}^{-1}) = +876.9 \text{ kJ}$

The final reactant, 2 Mg$_2$SiO$_4$ decomposes into elements as follows, and the enthalpy change will be twice the negative $\Delta H_m$

3 Mg$_2$SiO$_4$ → 6 O$_2$ + 6 Mg (s) + 2 Si(s) $\Delta H_5$ (5)

$\Delta H_5 = 3 \text{ mol} \times [-\Delta H_f[\text{Mg}_2\text{SiO}_4]] = 3 \text{ mol} \times [-\ (-2173.6 \text{ kJ mol}^{-1})] = +6520.8 \text{ kJ}$

Finally, we write the reaction for the formation of the product from elements:

6 Mg (s) + 4 Si(s) + 9 O$_2$ + 2 H$_2$O → 2 Mg$_3$Si$_2$O$_5$(OH)$_4$(s) $\Delta H_6$ (6)

$\Delta H_m = 2 \text{ mol} \times [\Delta H_f[\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4]] = 2 \text{ mol} \times [\ (-4360.3 \text{ kJ mol}^{-1})] = -8720.6 \text{ kJ}$

You can easily verify that the sum of Equations (3)-(6) is Equation (1).

Therefore

$\Delta H_{\text{net}} = \Delta H_3 + \Delta H_4 + \Delta H_5 + \Delta H_6$

$= +1143.2 \text{ kJ} + 876.9 \text{ kJ} + 6520.8 \text{ kJ} - 8720.6 \text{ kJ} = -179.7 \text{ kJ mol}$

Note carefully how Example 1 was solved. The reactant compounds Mg$_2$SiO$_4$(s) SiO$_2$(s) and H$_2$O(l) were hypothetically decomposed to its elements. These equations were the reverse of formation of the compounds, and so $\Delta H_f$ was opposite in sign from $\Delta H_f$. Step 1 also involved 4 mol H$_2$O(s) and so the enthalpy change had to be multiplied by 4.

In step 2, we had the hypothetical decomposition of SiO$_2$(s), with an enthalpy change which is the negative of $\Delta H_f$; finally, the hypothetical decomposition of 3 mol of Mg$_2$SiO$_4$ contributing 3 x $\Delta H_f$, and finally, we had the hypothetical formation of the product Mg$_3$Si$_2$O$_5$(OH)$_4$(s) from its elements. Since 2 mol were obtained, the enthalpy change was doubled but its sign remained the same.

Any chemical reaction can be approached similarly. To calculate $\Delta H_m$ we add all the $\Delta H_f$ values for the products, multiplying each by the appropriate coefficient, as in step 2 above. Since the signs of $\Delta H_f$ for the reactants had to be reversed in step 1, we subtract them, again multiplying by appropriate coefficients. This can he summarized by the equation

$\Delta H_m = \sum \Delta H_f$ (products) $- \sum \Delta H_f$ (reactants) (7) The symbol $\sum$ means “the sum of.” Since $\Delta H_f$ values are given per mole of compound, you must be sure to multiply each $\Delta H_f$ by an appropriate coefficient derived from the equation for which $\Delta H_m$ is being calculated.

Applying this equation to the Example we've just completed,

$\Delta H_m = [2 \text{ mol} \times -4360.6 \text{ kJ/mol}] - [3 \text{ mol} \times 2173.6 \text{ kJ/mol}] + (1 \text{ mol} \times -876.9 \text{ kJ/mol}) + (4 \text{ mol} \times -285.8 \text{ kJ/mol})] = -179.7 \text{ kJ}$.
This is the enthalpy change for the **reaction as written**, forming 2 mol of product.

### Heats of Formation that Cannot be Measured

In some cases, such as that of water, the elements will react directly to form a compound, and measurement of the heat absorbed serves to determine $\Delta H_f$. Quite often, however, elements do not react directly with each other to form the desired compound, and $\Delta H_f$ must be calculated by combining the enthalpy changes for other reactions. In the case of "aqueous silica", $\text{SiO}_2(aq)$, the species is not actually formed from $\text{Si}$ and $\text{O}_2$, yet its enthalpy of formation can be calculated from other known enthalpy changes, and used legitimately as long as the species is specified and well defined.

When silicates dissolve, they form $\text{H}_4\text{SiO}_4$ (silicic acid, sometimes written $\text{Si(OH)}_4$). We know the heat of formation of these silica solutions:

$$\text{Si}(s) + \text{O}_2(g) + 2 \text{H}_2(g) + \text{O}_2(g) \rightarrow \text{Si(OH)}_4(qtz) (l) \quad \Delta H_m = -1457.3 \text{ kJ mol}^{-1}[6][7] \quad (1)$$

And we know the enthalpy change for the reaction

$$2 \text{H}_2\text{O} (l) \rightarrow 2 \text{H}_2(g) + \text{O}_2(g) \quad \Delta H_m = 571.6 \text{ kJ mol}^{-1} \quad (2)$$

So combining the two, and viewing $\text{Si(OH)}_4(aq)$ as $\text{SiO}_2(aq)$+2 H$_2$O, we get a valid heat of formation for:

$$\text{Si}(s) + \text{O}_2(g) \rightarrow \text{SiO}_2(aq) (l) \quad \Delta H_m = -885.7 \text{ kJ mol}^{-1} \quad (8)$$

for the fictional species $\text{SiO}_2(aq)$ (dissolved $\text{SiO}_2$ with no Si-O-H bonds), and we can replace $\text{SiO}_2(qtz) + 2 \text{H}_2\text{O}(l) \ (\Delta H_f = -910.9 + 571.6 = 1457.3 \text{ kJ})$ with $\text{SiO}_2(aq) \ (\Delta H_f = -885.7 \text{ kJ})$ in geothermal equations. In other words, we could have written Equation (1) as

$$3 \text{Mg}_2\text{SiO}_4(s) + \text{Si(OH)}_4(aq) + 2 \text{H}_2\text{O}(l) \rightarrow 2 \text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4(s) \quad \Delta H_m = -179.7 \text{ kJ mol}^{-1}[8] \quad (25^\circ \text{C}, 1 \text{ atm pressure}) \quad (1b)$$

### Standard Enthalpy of Formation of Elements

One further point arises from the definition of $\Delta H_f$. The **standard enthalpy of formation for an element in its most stable state must be zero**. If we form oxygen from its elements, for example, we are talking about the reaction

$$\text{O}_2(g) \rightarrow \text{O}_2(g) \text{ Since the oxygen is unchanged, there can be no enthalpy change, and } \Delta H_f = 0 \text{ kJ mol}^{-1}.$$ 

### Tables of Standard Enthalpies of Formation

There are many sources of standard enthalpies of formation for geologically important species. A Wikipedia article has references to several of them. Several print compilations are available, including those cited in this exemplar [9].

Many include software that adjusts the values to the high pressures (hundreds of bars (or atmospheres) and temperatures required by geologists. For example, [FREED or THERBAL](http://www.gnu.org/software/freedom/) or [SUPCRT92](http://www.supercrt.org/).
Standard enthalpies of formation for some common compounds are given in the table below. These values may be used to calculate $\Delta H_m$ for any chemical reaction so long as all the compounds involved appear in the tables. To see how and why this may be done, consider the following example.

### Some Standard Enthalpies of Formation at 25°C.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta H_f$/kJ mol$^{-1}$</th>
<th>$\Delta H_f$/kcal mol$^{-1}$</th>
<th>Compound</th>
<th>$\Delta H_f$/kJ mol$^{-1}$</th>
<th>$\Delta H_f$/kcal mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgCl(s)</td>
<td>−127.068</td>
<td>−30.35</td>
<td>H$_2$O(g)</td>
<td>−241.818</td>
<td>−57.79</td>
</tr>
<tr>
<td>AgN$_3$(s)</td>
<td>+620.6</td>
<td>+148.3</td>
<td>H$_2$O(l)</td>
<td>−285.8</td>
<td>−68.3</td>
</tr>
<tr>
<td>Ag$_2$O(s)</td>
<td>−31.0</td>
<td>−7.41</td>
<td>H$_2$O$_2$(l)</td>
<td>−187.78</td>
<td>−44.86</td>
</tr>
<tr>
<td>Al$_2$O$_3$(s)</td>
<td>−1675.7</td>
<td>−400.40</td>
<td>H$_2$S(g)</td>
<td>−20.63</td>
<td>−4.93</td>
</tr>
<tr>
<td>Br$_2$(l)</td>
<td>0.0</td>
<td>0.00</td>
<td>HgO(s)</td>
<td>−90.83</td>
<td>−21.70</td>
</tr>
<tr>
<td>Br$_2$(g)</td>
<td>+30.907</td>
<td>+7.385</td>
<td>I$_2$(s)</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>C(s), graphite</td>
<td>0.0</td>
<td>0.00</td>
<td>I$_2$(g)</td>
<td>+62.438</td>
<td>+14.92</td>
</tr>
<tr>
<td>C(s), diamond</td>
<td>+1.895</td>
<td>+0.453</td>
<td>KCl(s)</td>
<td>−436.747</td>
<td>−104.36</td>
</tr>
<tr>
<td>CH$_4$(g)</td>
<td>−74.81</td>
<td>−17.88</td>
<td>KBr(s)</td>
<td>−393.798</td>
<td>−94.097</td>
</tr>
<tr>
<td>CO(g)</td>
<td>−110.525</td>
<td>−26.41</td>
<td>MgO(s)</td>
<td>−601.7</td>
<td>−143.77</td>
</tr>
<tr>
<td>CO$_2$(g)</td>
<td>−393.509</td>
<td>−94.05</td>
<td>NH$_3$(g)</td>
<td>−46.11</td>
<td>−11.02</td>
</tr>
<tr>
<td>C$_2$H$_2$(g)</td>
<td>+226.73</td>
<td>+54.18</td>
<td>NO(g)</td>
<td>+90.25</td>
<td>+21.57</td>
</tr>
<tr>
<td>C$_2$H$_4$(g)</td>
<td>+52.26</td>
<td>+12.49</td>
<td>NO$_2$(g)</td>
<td>+33.18</td>
<td>+7.93</td>
</tr>
<tr>
<td>C$_2$H$_6$(g)</td>
<td>−84.68</td>
<td>−20.23</td>
<td>N$_2$O$_4$(g)</td>
<td>+9.16</td>
<td>+2.19</td>
</tr>
<tr>
<td>C$_6$H$_6$(l)</td>
<td>+49.03</td>
<td>+11.72</td>
<td>NF$_3$(g)</td>
<td>−124.7</td>
<td>−29.80</td>
</tr>
<tr>
<td>CaO(s)</td>
<td>−635.09</td>
<td>−151.75</td>
<td>NaBr(s)</td>
<td>−361.062</td>
<td>−86.28</td>
</tr>
<tr>
<td>CaCO$_3$(s)</td>
<td>−1206.92</td>
<td>−288.39</td>
<td>NaCl(s)</td>
<td>−411.153</td>
<td>−98.24</td>
</tr>
<tr>
<td>CuO(s)</td>
<td>−157.3</td>
<td>−37.59</td>
<td>O$_3$(g)</td>
<td>+142.7</td>
<td>+34.11</td>
</tr>
<tr>
<td>Fe$_2$O$_3$(s)</td>
<td>−824.2</td>
<td>−196.9</td>
<td>SO$_2$(g)</td>
<td>−296.83</td>
<td>−70.93</td>
</tr>
</tbody>
</table>
Example 2

Use the table of standard enthalpies of formation at 25°C below to calculate $\Delta H_m$ for the reaction

Forsterite + water $\rightarrow$ serpentine (chrysotile) + brucite

$3 \text{Mg}_2\text{SiO}_4(s) + 3 \text{H}_2\text{O}(l) \rightarrow 2 \text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4(s) + \text{Mg(OH)}_2(s)$ $\Delta H_m=?$ (25°C, 1 atm pressure) (3)

<table>
<thead>
<tr>
<th></th>
<th>$\Delta H_f$ kJ mol$^{-1}$ *</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3 \text{Mg}_2\text{SiO}_4(s)$</td>
<td>-2173.6</td>
</tr>
<tr>
<td>$3 \text{H}_2\text{O}(l)$</td>
<td>-285.5</td>
</tr>
<tr>
<td>$2 \text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4(s)$</td>
<td>-4360.3</td>
</tr>
<tr>
<td>$\text{Mg(OH)}_2(s)$</td>
<td>-924.20</td>
</tr>
</tbody>
</table>

- values from SUPCRT$^{[11]}$

Solution

Using Eq. (4), we have

$\Delta H_m = \sum \Delta H_f$(products) $- \sum \Delta H_f$(reactants)

$\Delta H_m = [1 \text{ mol} \times \Delta H_f(\text{Mg(OH)}_2) + 2\text{ mol} \times \Delta H_f(\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4)] - [3 \text{ mol} \times \Delta H_f(\text{H}_2\text{O}) + 3 \text{ mol} \times \Delta H_f(\text{Mg}_2\text{SiO}_4)]$

$\Delta H_m = 1 \text{ mol}(-924.20) \text{ kJ mol}^{-1} + 2 \text{ mol}(-4360.3) \text{ kJ mol}^{-1} - 3(-285.8 \text{ kJ mol}^{-1}) - 3 \text{ mol} \times -2173.6 \text{ kJ mol}^{-1}$

$\Delta H_m = -924.20 \text{ kJ} - 8720.6 \text{ kJ} + 856.5 \text{ kJ} + 6520.8 \text{ kJ}$

$\Delta H_m = -2267 \text{ kJ}$

Reactions like this supply the large amounts of heat necessary to drive the thermal vents of the "Lost City".

Example 3

Use the table of standard enthalpies of formation at 25°C to calculate $\Delta H_m$ for the reaction

$4\text{NH}_3(g) + 5\text{O}_2(g) \rightarrow 6\text{H}_2\text{O}(g) + 4\text{NO}(g)$
Solution Using Eq. (4), we have

\[ \Delta H_m = \sum \Delta H_f \text{(products)} - \sum \Delta H_f \text{(reactants)} \]

\[ = [6 \Delta H_f (H_2O) + 4 \Delta H_f (NO)] - [4 \Delta H_f (NH_3) + 5 \Delta H_f (O_2)] \]

\[ = 6(-241.8) \text{ kJ mol}^{-1} + 4(90.3) \text{ kJ mol}^{-1} - 4(-46.1 \text{ kJ mol}^{-1}) - 5 \times 0 \]

\[ = -1450.8 \text{ kJ mol}^{-1} + 361.2 \text{ kJ mol}^{-1} + 184.4 \text{ kJ mol}^{-1} \]

\[ = -905.2 \text{ kJ mol}^{-1} \]

Note that we were careful to use \( \Delta H_f \:[H_2O(g)] \) not \( \Delta H_f \:[H_2O(l)] \). Even though water vapor is not the most stable form of water at 25°C, we can still use its \( \Delta H_f \) value. Also the standard enthalpy of formation of the element \( O_2(g) \) is zero by definition. Obviously it would be a waste of space to include it in the table above.

References

1. ↑ [http://en.Wikipedia.org/wiki/Lost_City_dermal_field%29](http://en.Wikipedia.org/wiki/Lost_City_dermal_field%29)
3. ↑ www.lostcity.washington.edu/file/lmax+
4. ↑ www.lostcity.washington.edu/f...+Cut+3863-1419

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