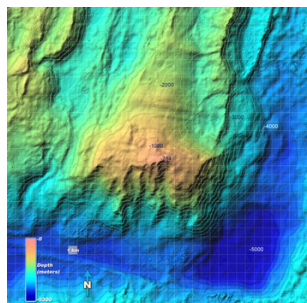# 3.10.3: Geology- Calculating the Heat Released by Serpentinization in the "Lost City"

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.

A topographic map of Atlantis Massif with many different shades of color to show the different depths of the area. A color bar legend is shown on the bottom left corner which corresponds to different depths.

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)

$3\ Mg_2SiO_4(s) + SiO_2(aq) + 4\ H_2O(l) \rightarrow 2\ Mg_3Si_2O_5(s)(OH)_4(s)$ (1)

We can use Hess' law to calculate the ΔH_m from a single list of **standard enthalpies of formation** ΔH_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

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ $\Delta H_m = -285.8$ 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 $H_2O(l)$ formed. Equation (1) must specify formation of *1* mol $H_2O(l)$, and so the coefficient of O_2 must be ½.

Example 1

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

Equation for Example 1			
	3 Mg$_2$SiO$_4$	+ SiO$_2$ (aq)	+ 4 H$_2$O →	2 Mg$_3$Si$_2$O$_5$(OH)$_4$
ΔH$_f$ kJ*mol^{-1}*	-2173.6	-876.9	-285.8	-4360.3

*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) ΔH$_3$= (3)
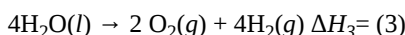
Since this is the *reverse* of formation of *4* mol H$_2$O(l) from its elements, the enthalpy change is

ΔH$_3$ = 4 mol × {−ΔH$_f$ [H$_2$O(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) ΔH$_4$ (4)
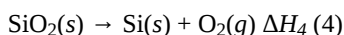
ΔH$_4$ = 1 mol × - ΔH$_f$ [SiO$_2$(g)] = 1 mol × -(− 876.9 kJ mol^{-1}) = + 876.9 kJ

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

3 Mg$_2$SiO$_4$ → 6 O$_2$ + 6 Mg (s) + 2 Si(s)ΔH$_5$ (5)
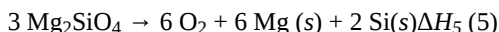
ΔH$_5$ = 3 mol × {−ΔH$_f$ [Mg$_2$SiO$_4$]} = 3 mol × [− (−2173.6 kJ mol^{-1})] = +6520.8 kJ

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) ΔH$_6$ (6)
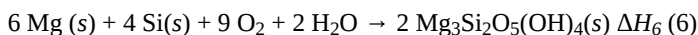
ΔH$_m$ = 2 mol × {ΔH$_f$ [Mg$_3$Si$_2$O$_5$(OH)$_4$]} = 2 mol × [(−4360.3 kJ mol^{-1})] = -8720.6 kJ You can easily verify that the sum of Equations (3)-(6) is Equation (1).

Therefore

ΔH$_{net}$ = ΔH$_3$ + ΔH$_4$ + ΔH$_5$+ ΔH$_6$

= +1143.2 kJ + 876.9 kJ +6520.8 kJ -8720.6 kJ = − 179.7 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 ΔH$_1$ was opposite in sign from ΔH$_f$. 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 ΔH$_f$; finally, the hypothetical decomposition of 3 mol of Mg$_2$SiO$_4$ contributing 3 x -ΔH$_f$, 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 ΔH$_m$ we *add* all the ΔH$_f$ values for the products, multiplying each by the appropriate coefficient, as in step 2 above. Since the signs of ΔH$_f$ 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

ΔH$_m$ = Σ ΔH$_f$ (products) − Σ ΔH$_f$ (reactants) (7) The symbol Σ means "the sum of." Since ΔH$_f$ values are given *per mole* of compound, you must be sure to multiply each ΔH$_f$ by an appropriate coefficient derived from the equation for which ΔH$_m$ is being calculated.

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

ΔH_m = [2 mol x -4360.6 kJ/mol] - [3 mol x 2173.6 kJ/mol) + (1 mol x -876.9 kJ/mol) + (4 mol x -285.8 kJ/mol)] = -179.7 kJ.

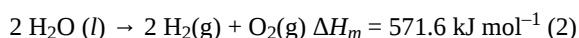This is the enthalpy change for the *reaction as written*, forming 2 mol of product.

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 ΔH_f. Quite often, however, elements do not react directly with each other to form the desired compound, and ΔH_f must be calculated by combining the enthalpy changes for other reactions. In the case of "aqueous silica", $SiO_2(aq)$, the species is not actually formed from Si and 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 H_4SiO_4 (silicic acid, sometimes written $Si(OH)_4$). We know the heat of formation of these silica solutions:

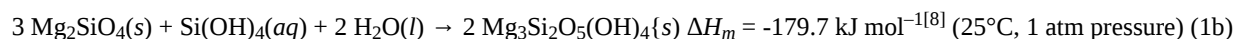$Si(s) + O_2(g) + 2 H_2(g) + O_2(g) \rightarrow Si(OH)_4(qtz)$ (l) ΔH_m = -1457.3 kJ mol^{-1}[6][7] (1)
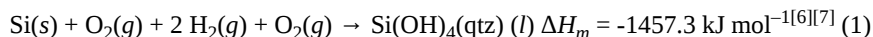
And we know the enthalpy change for the reaction

$2 H_2O$ (l) $\rightarrow$ 2 $H_2(g)$ + $O_2(g)$ ΔH_m = 571.6 kJ mol^{-1} (2)

So combining the two, and viewing $Si(OH)_4(aq)$ as $SiO_2(aq)$•2 H_2O, we get a valid heat of formation for :

$Si(s) + O_2(g) \rightarrow SiO_2$(aq) (l) ΔH_m = -885.7 kJ mol^{-1} (8)
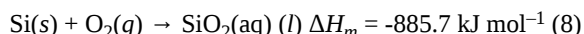
for the fictional species SiO_2(aq) (dissolved SiO_2 with no Si-O-H bonds), and we can replace $SiO_2(qtz)$ + 2 $H_2O(l)$ (ΔH_f = -910.9 + 571.6 = 1457.3 kJ) with SiO_2(aq) (ΔH_f = -885.7 kJ) in geothermal equations. In other words, we could have written Equation (1) as

$3 Mg_2SiO_4(s) + Si(OH)_4(aq) + 2 H_2O(l) \rightarrow 2 Mg_3Si_2O_5(OH)_4\{s\}$ ΔH_m = -179.7 kJ mol^{-1}[8] (25°C, 1 atm pressure) (1b)

Standard Enthalpy of Formation of Elements

One further point arises from the definition of ΔH_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

$O_2(g) \rightarrow O_2(g)$ Since the oxygen is unchanged, there can be no enthalpy change, and ΔH_f = 0 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 or SUPCRT92[10].

Standard enthalpies of formation for some common compounds are given in the table below. These values may be used to calculate ΔH_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.

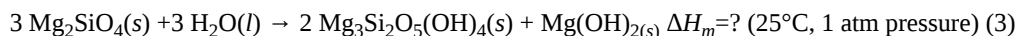Some Standard Enthalpies of Formation at 25°C.

Compound	ΔH_f/kJ mol^{-1}	ΔH_f/kcal mol^{-1}	Compound	ΔH_f/kJ mol^{-1}	ΔH_f/kcal mol^{-1}
AgCl(s)	−127.068	−30.35	$H_2O(g)$	−241.818	−57.79
$AgN_3(s)$	+620.6	+148.3	$H_2O(l)$	−285.8	−68.3
$Ag_2O(s)$	−31.0	−7.41	$H_2O_2(l)$	−187.78	−44.86
$Al_2O_3(s)$	−1675.7	−400.40	$H_2S(g)$	−20.63	−4.93
$Br_2(l)$	0.0	0.00	HgO(s)	−90.83	−21.70

Compound	ΔH_f/kJ mol^{-1}	ΔH_f/kcal mol^{-1}	Compound	ΔH_f/kJ mol^{-1}	ΔH_f/kcal mol^{-1}
$Br_2(g)$	+30.907	+7.385	$I_2(s)$	0.0	0.0
$C(s)$, graphite	0.0	0.00	$I_2(g)$	+62.438	+14.92
$C(s)$, diamond	+1.895	+0.453	$KCl(s)$	–436.747	–104.36
$CH_4(g)$	–74.81	–17.88	$KBr(s)$	–393.798	–94.097
$CO(g)$	–110.525	–26.41	$MgO(s)$	–601.7	–143.77
$CO_2(g)$	–393.509	–94.05	$NH_3(g)$	–46.11	–11.02
$C_2H_2(g)$	+226.73	+54.18	$NO(g)$	+90.25	+21.57
$C_2H_4(g)$	+52.26	+12.49	$NO_2(g)$	+33.18	+7.93
$C_2H_6(g)$	–84.68	–20.23	$N_2O_4(g)$	+9.16	+2.19
$C_6H_6(l)$	+49.03	+11.72	$NF_3(g)$	–124.7	–29.80
$CaO(s)$	–635.09	–151.75	$NaBr(s)$	–361.062	–86.28
$CaCO_3(s)$	–1206.92	–288.39	$NaCl(s)$	–411.153	–98.24
$CuO(s)$	–157.3	–37.59	$O_3(g)$	+142.7	+34.11
$Fe_2O_3(s)$	–824.2	–196.9	$SO_2(g)$	–296.83	–70.93
$HBr(g)$	–36.4	–8.70	$SO_3(g)$	–395.72	–94.56
$HCl(g)$	–92.307	–22.06	$ZnO(s)$	–348.28	–83.22
$HI(g)$	+26.48	+6.33			

Example 2

Use the table of standard enthalpies of formation at 25°C below to calculate ΔH_m for the reaction

Forsterite + water → serpentine (chrysotile) + brucite

$3\ Mg_2SiO_4(s) + 3\ H_2O(l) \rightarrow 2\ Mg_3Si_2O_5(OH)_4(s) + Mg(OH)_{2(s)}$ ΔH_m=? (25°C, 1 atm pressure) (3)

	Equation for Example 2			
	$3\ Mg_2SiO_4(s)$	$+ 3\ H_2O(l) \rightarrow$	$2\ Mg_3Si_2O_5(OH)_4(s)$	$+ Mg(OH)_2(s)$
ΔH_f kJ mol^{-1} *	-2173.6	-285.5	-4360.3	-924.20

- values from SUPCRT[11]

Solution

Using Eq. (4), we have

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

$\quad = [1 \text{ mol x } \Delta H_f (Mg(OH)_2) + 2\text{mol x } \Delta H_f (Mg_3Si_2O_5(OH)_4)] - [3 \text{ mol x } \Delta H_f (H_2O) + 3 \text{ mol x } \Delta H_f (Mg_2SiO_4)]$

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

$\quad = –924.20 \text{ kJ -8720.6 kJ} + 856.5 \text{ kJ} + 6520.8 \text{ kJ}$

$\quad = \text{-2267 kJ}$

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 ΔH_m for the reaction

$4NH_3(g) + 5O_2(g) \rightarrow 6H_2O(g) + 4NO(g)$

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 ΔH_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. ↑ Lost City [en.Wikipedia.org]
2. ↑ Geology [www.lostcity.washington.edu]
3. ↑ www.lostcity.washington.edu/file/Imax+
4. ↑ www.lostcity.washington.edu/f...+Cut+3863-1419
5. ↑ GEOPIG Supcrt Application Reactants [geopig3.la.asu.edu:8080]
6. ↑ Nordstrom, D.K.; Munoz, J.L. "Geochemical Thermodynamics", 2nd Ed., Blackwell Scientific Publishers, Boston,1994, p. 442
7. ↑ Nordstrom, D.K.; Plummer, L.N.; Langmuir, D., et al. "Revised chemical equilibrium data for major water-mineral reactions and their limitations." In Chemical massett, pp. 398-413. American Chemical Society Symposium Series 416.
8. ↑ values from SUPCRT. GEOPIG Supcrt Application Reactants [geopig3.la.asu.edu:8080]
9. ↑ Robie, R. A.; Hemingway, B.S. "Thermodynamic Properties of Minerals and Related Substances at 298.15 K and 1 Bar (10^5 Pascals) Pressure and at Higher Temperatures." U.S. Geological Survey Bulletin 2131, U.S. Government Printing Office, Washington, DC: 1995.
10. ↑ GEOPIG Supcrt Application Reactants [geopig3.la.asu.edu:8080]
11. ↑ GEOPIG Supcrt Application Reactants [geopig3.la.asu.edu:8080]