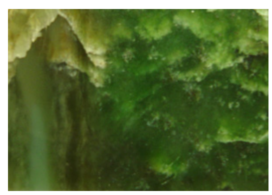
3.8.4: Geology- Heat Engine at Lost City

The Earth's mantle is composed largely of *ultramafic rock* which has high Fe or Mg content, and low silicon content. This rock may be converted to *"serpentinites"* by a process (logically) called *serpentinization"*, which is an ***exothermic*** process, releasing a lot of heat energy-- about 660,000,000 joules of heat per cubic meter of rock according to the NOAA (National Oceanic and Atmospheric Administration). This is enough energy to raise the temperature of the rock by 260°C (550°F)[1]. The "Lost City", located 20 km west of the Mid-Atlantic Ridge, is a hydrothermal vent field characterized by carbonate edifices that tower 60 m above the ocean floor and extreme conditions found nowhere else in the marine environment[2]

Serpentinites at Lost City. Photo taken with the robotic vehicle Hercules. The wreckfish is ~ 1 m in length[3]

Serpentine itself is often chrysotile, $Mg_3Si_2O_5(OH)_4$. The name "serpentine" derives from the Latin *serpentinus* ("serpent rock") because the mineral is often greenish with a smooth to scaly surface[4].

 Serpentine	 Polished Serpentine Sample

Serpentine marbles are used in architecture and jewelry, but other serpentines include asbestos (which is a lung cancer risk when mined) and another 20 varieties of hydrous magnesium/iron phyllosilicates. Serpentinites often are toxic to plants because they may contain significant levels of nickel, chromium, and cobalt. They are often mixed, and thus treated collectively as a group called "serpentinites."

In the case of the "Lost City" of hydrothermal vents in the mid-Atlantic, serpentinization is a greater source of energy than the radioactivity of the Earth's core . Radioactivity normally accounts for about 80% of the internal heat of the Earth [5]. But ***Thermochemical reactions*** like serpentinization, which produce or consume significant amounts of heat, are an inextricable part of all geological processes.

Thermochemical Equations

Since serpentinites are mixtures, several equations can be used to describe their reactions. While natural minerals may have indefinite compositions like olivine, $(Fe,Mg)_2SiO_4$, we always look at equations for specific reactions in order to associate definite energies with them. These are called **thermochemical equations**. For example, serpentinization may involve:

Fayalite + water → magnetite + aqueous silica + hydrogen

$3\ Fe_2SiO_4 + 2\ H_2O \rightarrow 2\ Fe_3O_4 + 3\ SiO_2 + 3\ H_2$ $\Delta H_m = 40.1$ kJ[6] (25°C, 1 atm pressure) (1)

Or: Forsterite + aqueous silica → serpentine (crysotile)

$3\ Mg_2SiO_4 + SiO_2 + 4\ H_2O \rightarrow 2\ Mg_3Si_2O_5(OH)_4$ $\Delta H_m = -179.7$ kJ[7] (25°C, 1 atm pressure) (2)

Or: Forsterite + water → serpentine (chrysotile) + brucite

$3\ Mg_2SiO_4 + 3\ H_2O \rightarrow 2\ Mg_3Si_2O_5(OH)_4 + Mg(OH)_2$ ΔH_m = -2267.2 kJ[8] (25°C, 1 atm pressure) (3)

Here the ΔH_m (delta *H* subscript m) tells us whether heat energy is released or absorbed when the reaction occurs and also enables us to find the actual quantity of energy involved. By convention, if ΔH_m is *positive*, as in Equation (1), heat is *absorbed* by the reaction; i.e., it is **endothermic**. More commonly, ΔH_m is *negative* as in Eq. (2), indicating that heat energy is *released* rather than absorbed by the reaction, and that the reaction is **exothermic**. This convention as to whether ΔH_m is positive or negative looks at the heat change in terms of the matter actually involved in the reaction rather than its surroundings. In the reaction in Eq. (2), the strength of the bonds increases as products are formed, so the products are lower in potential energy, and the lost energy is indicated by a negative value of ΔH_m.

The values are calculated, as we'll see later, from standard tabulated values found in databases developed especially for geologists[9] [10] [11] [12]

It is important to notice that ΔH_m is the energy for the reaction as written. The quantity of heat released or absorbed by a reaction is proportional to the amount of each substance consumed or produced by the reaction. Thus Eq. (2) tells us that 179.7 kJ of heat energy is given off *for every mole* of SiO_2 which is consumed, or for every 3 mol of Mg_2SiO_4 consumed. Alternatively, it tells us that 179.7 kJ is released *for every 2 moles of* $Mg_3Si_2O_5(OH)_4$ produced. Seen in this way, ΔH_m is a conversion factor enabling us to calculate the heat absorbed when a given amount of substance is consumed or produced. If q is the quantity of heat absorbed and n is the amount of substance involved, then:

$\Delta H_{\mathrm{m}} = \frac{q}{n}$ (4)

EXAMPLE 1

How much heat energy is obtained when 1 kg of the serpentine chrysotile, $Mg_3Si_2O_5(OH)_4$, is formed according to Equation (2)?

Solution

The mass of $Mg_3Si_2O_5(OH)_4$ is easily converted to the amount of $Mg_3Si_2O_5(OH)_4$ from which the heat energy q is easily calculated by means of Eq. (4). The value of ΔH_m is –179.7 kJ per 2 moles of $Mg_3Si_2O_5(OH)_4$. The road map is:

$m_{\mathrm{Mg_2Si_2O_5OH_4}} \xrightarrow{M} n_{\mathrm{Mg_2Si_2O_5OH_4}} \xrightarrow{\Delta H_m} q$ so that $q = 1 \times 10^3\ \mathrm{g\ Mg_2Si_2O_5(OH)_4} \times \frac{1\ \mathrm{mol\ Mg_2Si_2O_5(OH)_4}}{277.112\ \mathrm{g\ Si_2O_5(OH)_4}} \times \frac{-179.7 kJ}{2\ \mathrm{mol\ Mg_2Si_2O_5(OH)_4}}$ = q = -324 kJ Note: By convention a negative value of q corresponds to a release of heat energy by the matter involved in the reaction. The quantity ΔH_m is the **enthalpy change as the reaction proceeds as written**. In this context the symbol Δ (delta) signifies change in" while *H* is the symbol for the quantity being changed, namely the enthalpy. We will deal with the enthalpy in some detail in Chap. 15. For the moment we can think of it as a property of matter which increases when matter absorbs energy and decreases when matter releases energy.

It is important to realize that the value of ΔH_m given in thermochemical equations like (1), (2) or (3) depends on the physical state of both the reactants and the products. Thus, if water were present as a gas instead of a liquid in the reaction in Eq. (1), the value of ΔH_m would be different from 40.1 kJ. These reactions may occur under conditions where water may be supercritical (above 374°C) and yet a different value would be obtained. It is also necessary to specify both the temperature and pressure since the value of ΔH_m depends very slightly on these variables. If these are not specified [as in Eq. (3)] they usually refer to 25°C and to normal atmospheric pressure. Since geochemical processes like those above normally occur at hundreds of atmospheres (hundreds of bars) pressure and elevated temperatures, geologists adjust the standard enthalpies to give values appropriate for the conditions. Although the adjustments are not difficult, computer programs exist to do the work.

Forward and Reverse Thermochemical Equations

Another characteristic of thermochemical equations arise from the law of conservation of energy. The first is that *writing an equation in the reverse direction changes the sign of the enthalpy change.*

Calcite/Aragonite

For example[13], the conversion of the two forms of calcium carbonate

$CaCO_3 \Leftrightarrow CaCO_3$ ΔH_m = -0.17 kJ (5)

calcite aragonite

Therefore, the forward direction (calcite to aragonite) is exothermic, releasing heat as a more stable crystal lattice forms. Logically, in the reverse direction, disrupting the stable lattice of aragonite must require energy, so the conversion of aragonite to calcite endothermic:

$CaCO_3 \Leftrightarrow CaCO_3$ ΔH_m = +0.17 kJ (6)
aragonite calcite

Water/Ice

Melting or freezing water can release or absorb significant amounts of heat:

$H_2O(l) \rightarrow H_2O(g)$ ΔH_m = 44 kJ (7)

tells us that when a mole of liquid water vaporizes, 44 kJ of heat is absorbed. This corresponds to the fact that heat is absorbed from your skin when perspiration evaporates, and you cool off. Condensation of 1 mol of water vapor, on the other hand, gives off exactly the same quantity of heat.

$H_2O(g) \rightarrow H_2O(l)$ ΔH_m = –44 kJ (8)

To see why this must be true, suppose that ΔH_m [Eq. (7)] = 44 kJ mol while ΔH_m [Eq. (8)] = –50.0 kJ. If we took 1 mol of liquid water and allowed it to evaporate, 44 kJ would be absorbed. We could then condense the water vapor, and 50.0 kJ would be given off. We could again have 1 mol of liquid water at 25°C but we would also have 6 kJ of heat which had been created from nowhere! This would violate the law of conservation of energy. The only way the problem can he avoided is for ΔH_m of the reverse reaction to be equal in magnitude but opposite in sign from ΔH_m of the forward reaction. That is, ΔH_m forward = –ΔH_m reverse

References

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