

Thermodynamic constraints on chemolithotrophic metabolism at hydrothermal vents

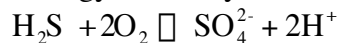
Hydrothermal vents are systems that occur when water is present in a steep geothermal gradient. Familiar examples are the geysers of Yellowstone National Park, and the ‘black smokers’ at mid-ocean ridges. The geothermal energy heats the vent water to high temperatures: in the case of black smokers the water may be as hot as 350°C.

These systems are interesting because they support a variety of life that ultimately derives its energy from **chemosynthesis** rather than photosynthesis. Organisms generate energy by taking advantage of thermodynamic disequilibrium between reduced vent water (in equilibrium with the rock beneath the seafloor) and oxidized seawater.

Microorganisms living at the highest temperature vents are known as **hyperthermophiles**. They thrive at 80° to 105°C. These organisms have unique enzymes that allow them to live at very high temperatures. These organisms are especially interesting from an evolutionary point of view, because when one examines the universal phylogenetic tree of life, all of the most primitive branches are occupied by hyperthermophiles.

It is possible then that studying these organisms may help us better understand early evolution of life on Earth. Hyperthermophiles potentially play a role in forming rock textures and mineral assemblages that are diagnostic for life in ancient rocks on Earth and possibly also on Mars. Hyperthermophiles may help us understand the evolution of a variety of metabolic pathways and the conditions under which life is possible.

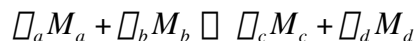
One of the questions to be addressed is how to determine what kind of metabolic pathways might be available to organisms living at hydrothermal vents using chemosynthesis. An organism may extract metabolic energy from a chemical reaction if it results in a lowered Gibbs free energy for the system. For example sulfide oxidation



may be favorable under certain conditions of temperature and concentrations of the species involved.

Ideally, we would like a way to find out how much energy is available in a chemical system based on the concentrations of the species involved and on the temperature.

For a general reaction we can write



where the ν_i 's are stoichiometric coefficients and M_i 's are species.

As the reaction progresses,

$$\frac{\nu_a N_a}{\nu_a} = \frac{\nu_b N_b}{\nu_b} = \frac{\nu_c N_c}{\nu_c} = \frac{\nu_d N_d}{\nu_d}.$$

Taking the infinitesimally small change, we can define $\frac{dN_i}{\nu_i} = d\xi$ where ξ is the 'reaction progress variable'.

We also know that

$$dG = SdT + VdP + \sum_{i=1}^C \nu_i dN_i.$$

By substitution

$$dG = SdT + VdP + \left(\sum_{i=1}^C \nu_i \nu_i \right) d\xi$$

and therefore

$$\left(\frac{\partial G}{\partial \xi} \right)_{T,P} = \sum_{i=1}^C \nu_i \nu_i$$

The **chemical affinity** $A = - \left(\frac{\partial G}{\partial \xi} \right)_{T,P}$ describes the extent to which a system is out of equilibrium. It can also be written as

$$A = RT \log(K_r / Q_r)$$

where $Q_r = \prod a_i^{\nu_i}$ is the activity product. The activity product is related to the concentration of each species in the mixed vent water and seawater. This definition of chemical affinity allows us to convert the concentrations of species in a system that is out of equilibrium to the amount of energy available. The calculation is complicated by the fact that both K_r and Q_r are dependant on temperature.

For the previous reaction we see that sulfate reduction has a positive affinity (will provide energy) above 38°C, and available energy is maximized at about 80°C. Taking this approach could predict likely avenues of chemosynthesis on the early Earth and on Mars.

