CHNOSZ

Gallery of CHNOSZ calculations

1 Purpose

The purpose of this gallery is to demonstrate a range of calculations for inorganic, organic and protein systems using CHNOSZ.

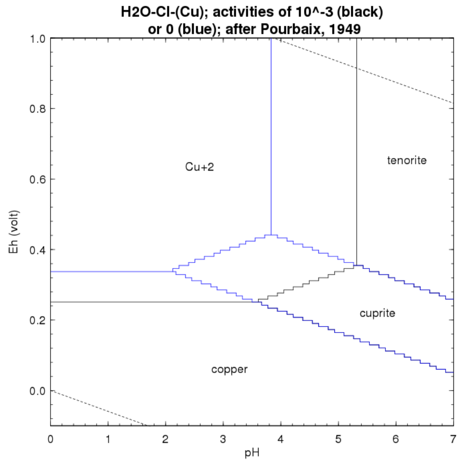
The R software environment is a nice platform for thermodynamic calculations not only for its mathematical and graphical features but also because the documentation of a package like CHNOSZ can include both technical details and worked-out examples. The script for each of the examples below is part of the CHNOSZ documentation, and can be viewed by clicking on any of the figures in the HTML version of this document.

The PDF version of this document can be found here[1] .

2 Inorganic examples

2.1 Eh-pH equal activity diagram

It is a snap to make Pourbaix diagrams in CHNOSZ. This one shows the stability fields of solid copper, cuprite (Cu2O), tenorite (CuO) and aqueous Cu+2 and CuCl. It is inspired by a diagram in Pourbaix, 1949[2] [1].



The base diagram was drawn for activities of the aqueous species set to 10^{-3} and the blue lines that are overlaid show the predominance field boundaries when the aqueous species activities are unity. The dashed lines are the upper and lower stability limits of H_2O.

2.2 Temperature-pressure phase diagram

It is just as easy to make temperature-pressure or other types of activity diagrams in CHNOSZ. This is a classic system that is often used to illustrate the Clapeyron slope.

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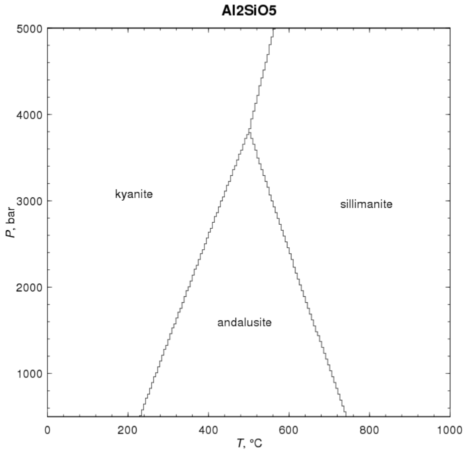
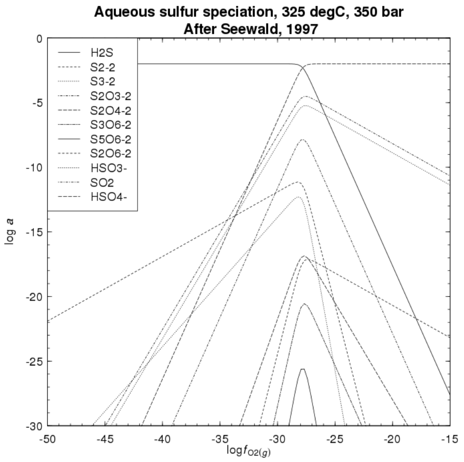
[1] http://www.chnosz.net/gallery/gallery.pdf

[2] http://www.worldcat.org/oclc/1356445



2.3 Sulfur speciation

The distribution of aqueous sulfur species as a function of oxygen fugacity is shown below. This diagram was produced in CHNOSZ to imitate a figure presented by Seewald, 1997 [2].



3 Organic examples

3.1 Eh-pH predominance diagram

Here is an Eh-pH diagram for the amino acid cysteine, its anion cysteinate, and the neutral disulfide cystine. Oxidizing conditions generally favor the formation of disulfide bonds in proteins; the stabilization of the disulfide bond may prevent the formation of the anionic (cysteinate) form of the sidechain group, hence raising the net charge of some proteins (Dick et al., 2006[3]) [3].

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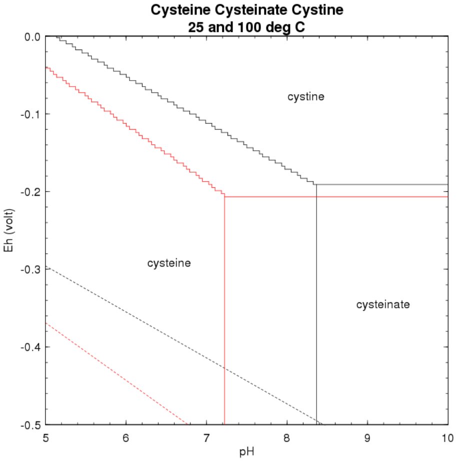
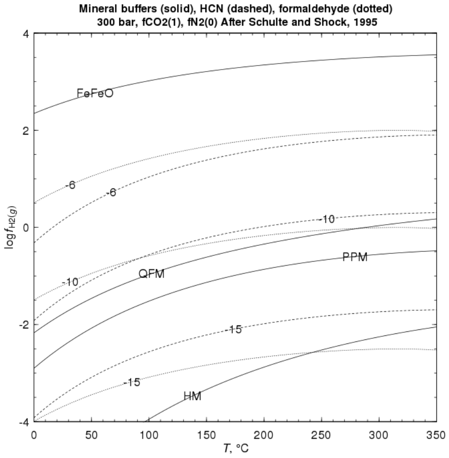
[3] http://www.biogeosciences.net/3/311/2006/bg-3-311-2006.html



An advantage of using CHNOSZ is that the revised Helgeson-Kirkham-Flowers equations of state for aqueous species are integral to the code and permit the rapid calculation of stability diagrams at elevated temperatures. In the figure above, the location of the triple point moves toward lower pH and Eh at 100 °C, and the water reduction stability limit (dashed lines) also changes with temperature.

3.2 Hydrothermal buffers

CHNOSZ can be used to replicate many types of thermodynamic calculations presented in the literature for organic systems. The following diagram is the CHNOSZ-ified version of a figure from Schulte and Shock, 1995[4] [4] showing the hydrogen fugacity as a function of temperature for a number of mineral buffers and of synthesis reactions of hydrogen cyanide (HCN) and formaldehyde (HCHO).



3.3 Nucleobase-amino acid interaction

The following diagram shows the stability fields of some nucleobases and the corresponding amino acids coded by the homocodonic triplets as a function of Eh and of logarithm of activity of H_2O (a way of quan-

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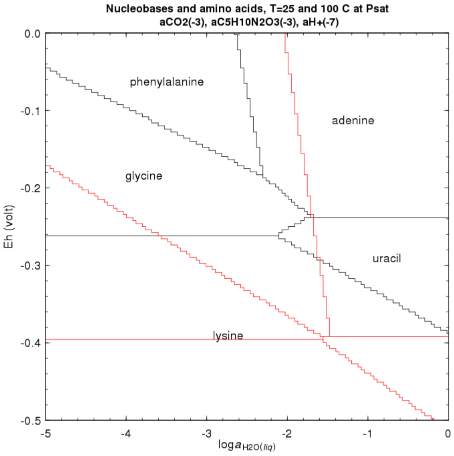
[4] http://www.ncbi.nlm.nih.gov/pubmed/11536668

tifying the hydration state). The requisite standard molal Gibbs energies and equations of state parameters were taken from Ref. [3] and LaRowe and Helgeson, 2006[5] [5].



Two speculations are informed by this diagram: 1) the formation of amino acids at the expense of the conjugate nucleobases is favored by decreasing activity of H2O at constant redox potential; 2) increasing the temperature to 100 °C raises the probability that a number of different amino acids and nucleobases coexist in metastable equilibrium.

4 Protein examples

4.1 Protein speciation

The diagram below shows the calculated relative abundances of selected surface-layer proteins as a function of oxygen fugacity that was adapted from a figure in Dick, 2008[6] [6]. The proteins from hyperthermophilic organisms such as *Methanocaldococcus jannaschii* (METJA) tend to be chemically stabilized by reducing conditions while those from mesophilic organisms such as *Methanococcus voltae* (METVO) and *Haloarcula japonica* (HALJP) are stabilized by relatively oxidizing conditions.

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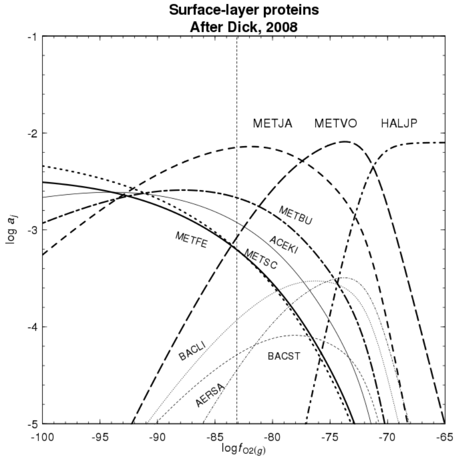
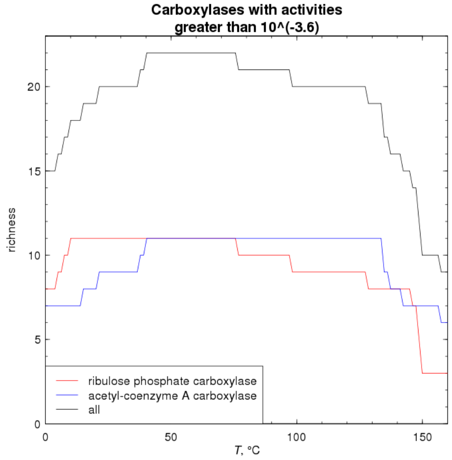
[5] http://dx.doi.org/10.1016/j.gca.2006.04.010

[6] http://www.geochemicaltransactions.com/content/9/1/10



4.2 Diversity calculations

The speciation diagram above shows that the relative abundances of chemical species in metastable equilibrium is a function of environmental properties such as $\log f_{O_{2(g)}}$. The calculated richness, or number of species whose activities are above a certain level, is shown below as a function of temperature for a different chemical system. This system contains 12 RuBisCOs and 12 acetyl coenzyme-A carboxylases from different organisms. The redox state as a function of temperature is buffered by the reduced and oxidized (disulfide) glutathione system and the carbonation state as a function of temperature by the solubility of carbon dioxide.



The chemical richness maximizes at moderate values of temperature. This outcome is perhaps reminiscent of high diversities at intermediate productivity levels observed in some natural systems (see e.g. Irigoien et al., 2004[7] [7]). The figure also shows that distinctive temperature ranges support coexistence of the proteins in each group.

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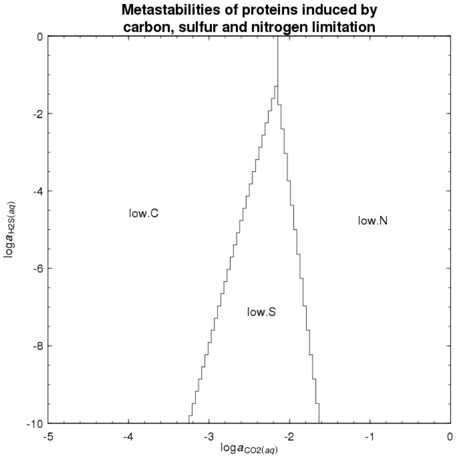
[7] http://dx.doi.org/10.1038/nature02593

4.3 Stress response

Sulfur limitation in yeast cultures promotes the formation of proteins with lower sulfur content (Boer et al., 2003[8] [8]). A multidimensional thermodynamic analysis might illuminate the interaction of different environmental parameters on the stress response reactions of proteomes. One way of tackling this problem using CHNOSZ is to create stability diagrams for the proteins that have been found to be induced or repressed under different stressful situations. The first plot below shows the relative metastability fields for proteins induced in yeast by carbon, nitrogen and sulfur limitation as a function of logarithm of activity of carbon dioxide (CO_2) and hydrogen sulfide (H_2S) (based on experimental protein expression data from Ref. [8]).



Note in the figure above the existence of a triple point, around which are located the fields representing proteins induced by various limiting conditions, and that the relative positions of these fields is consistent with the differences in environmental conditions imposed by the laboratory experiments. The next plot shows the relative metastability fields for proteins induced and repressed by carbon limitation under aerobic and anaerobic conditions and is based on experimental protein expression data from Tai et al., 2005[9] [9]. In this figure there are two triple points on a logarithm of hydrogen fugacity- logarithm of activity of glucose projection.

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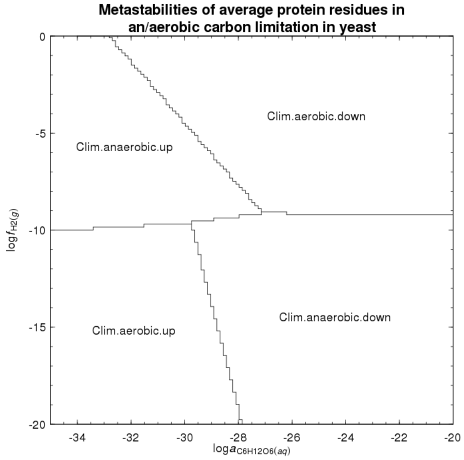
[8] http://www.ncbi.nlm.nih.gov/pubmed/12414795

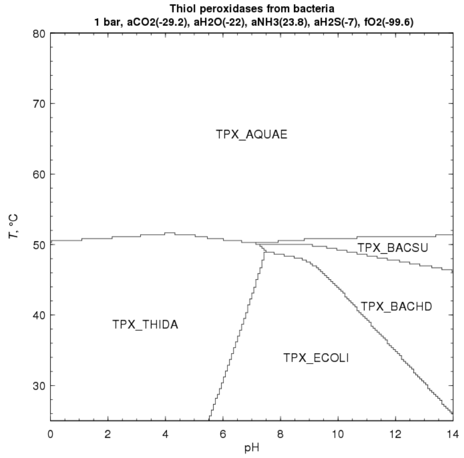
[9] http://www.ncbi.nlm.nih.gov/pubmed/15496405



The stability fields for the proteins that are up-regulated by glucose limitation occupy the low $\log a_{C_6H_{12}O_{6(aq)}}$ portion of the diagram. The stability fields for the proteins that are induced under aerobic conditions, or repressed by anaerobic conditions, occupy the oxidizing (low $\log f_{H_{2(g)}}$) portion of the diagram, and vice versa.

4.4 Buffers

The diagram below shows the stability fields of related proteins in five different bacterial organisms as a function of temperature and pH. The relative positions of the fields on this diagram is entirely a function of the chemical formulas and thermodynamic properties of the proteins. The fields all come together in a pseudoinvariant point because CHNOSZ was instructed to make a buffer out of all five proteins, which as a result constrains the activities of four of the basis species (CO2, H2O, NH3, O2) in the system.



Aquifex aeolicus (AQUAE) is a hyperthermophile; its thiol peroxidase appears to be chemically more stable at higher temperatures than the other thiol peroxidases shown here. *Thiobacillus denitrificans* (THIDA) is related to an acidophilic group of organisms (Schippers, 2004[10] [10]) and its thiol peroxidase is stabilized relative to those of the other organisms shown here by lower pHs. Likewise, the stability field for the thiol peroxidase from the alkaliphile *Bacillus halodurans* (BACHD) is in the high-pH region of the diagram.

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[10] http://dx.doi.org/10.1130/0-8137-2379-5.49

References

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