Getting started with CHNOSZ

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1 Introduction

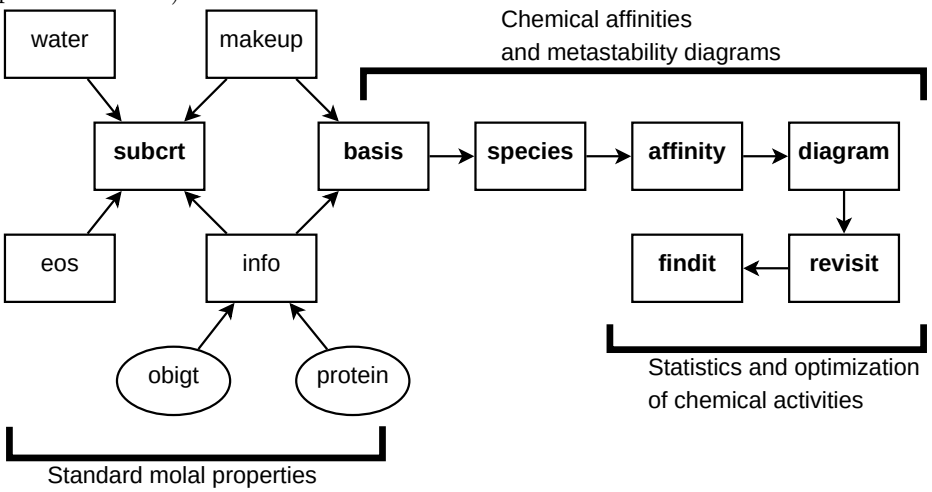
This document will orient you to the basic functionality of CHNOSZ, a package for the R software environment. R is a powerful language and also very fun to use. Don't worry if you're new to it; just plow through the examples below and you'll start to get the hang of it. If you want a more structured approach to learning the language, there are some excellent guides in the Manuals section of the R Project page. You may also want to refer to a publication on CHNOSZ itself [3].

The package was developed starting in 2003 to support a research project on the thermodynamic properties of proteins. Since that time, the functions in the package have expanded to include calculation of the thermodynamic properties of reactions, and especially the construction of chemical activity diagrams for both inorganic and organic systems. The development of the package since 2009 has focused on the calculation of the metastable equilibrium relative abundances of large numbers of proteins with applications in interpretation of metagenomic data and protein expression profiles.

Although I use the package primarily to model the relative stabilities of proteins in cells and in hydrothermal systems, the database and functions are flexible in their use. As you will see below, examples taken from low-temperature geochemistry are used to demonstrate, and indeed test, the package.

2 Outline of workflow

CHNOSZ is made up of a set of functions and supporting datasets. The major components of the package are shown in the figure below, which is a modified version of the flowchart shown in Ref. [3] (boxes – functions; ellipses – datasets).



Some common usage scenarios are:

- using `info()` to search for species in the thermodynamic database
- using `subcrt()` to calculate the thermodynamic properties of species and reactions

- using the sequence `basis()`, `species()`, `affinity()`, `diagram()` to assign the basis species that define the dimensions of chemical composition in a system, define the species of interest for relative stability calculations, calculate the affinities of formation reactions of the species of interest under reference (non-equilibrium) conditions, and to transform the non-equilibrium affinities to equilibrium chemical activities and plot the results.
- using `revisit()` to calculate/plot statistics of the chemical activities of the species of interest and `findit()` to search for combinations of activities of basis species, temperature and/or pressure that optimize those statistics. (These features, appearing in version 0.9-3 of the package, are not covered in this document.)

The functions are designed with an interactive setting in mind; you can make good use of CHNOSZ without having to write your own scripts. The examples in this vignette are meant to portray a simple interactive session. However, as you become more familiar with CHNOSZ and R, you will probably find it helpful to save sequences of function calls that produce interesting results. The results can then be reproduced on demand by yourself or others with whom you might share your scripts.

3 Installing and loading CHNOSZ

If you have just installed R, and you are online, installing the CHNOSZ package should be as simple as selecting "Install packages from CRAN" or similar menu item in the R GUI or using the following command to start the package installation process. (If you are not online, you instead have to tell R to install the package from a local package file.)

```
> install.packages("CHNOSZ")
```

Then load the CHNOSZ package to make its functions and data available in your working session.

```
> library(CHNOSZ)
```

```
CHNOSZ version 0.9-3 (2010-12-21)
thermo$obigt has 1782 aqueous, 2811 total species
```

The rest of this document assumes that the CHNOSZ package is loaded.

4 Thermodynamic database

4.1 `info()` part I

So you want to know what are the standard molal thermodynamic properties and equations of state parameters of aqueous ethylene? Look no further than the `info()` function, which provides a convenient interface to retrieve entries from the thermodynamic database packaged with CHNOSZ.

```
> info("ethylene")
```

```
info: ethylene (C2H4) available in aq, gas.
info: 88 refers to ethylene, C2H4 aq (SH90, 4.Sep.87)
```

There are two species named "ethylene" in the database. Normally, `info()` gives preference to aqueous species if they exist, so in this case we find that aqueous ethylene is species number 88 in the database. Let's display this entry, now by giving the numeric value to the function.

```
> info(88)
```

```
       name abbrv formula state source1 source2     date     G    H    S   Cp    V     a1
88 ethylene  <NA>    C2H4    aq    SH90    <NA> 4.Sep.87 19450 8570 28.7 62.5 45.5 0.7856
        a2      a3     a4   c1    c2  omega Z
88 1263.91 -1.8737 -33014 39.1 97000 -40000 0
```

If you were instead interested in the properties of the gas, you could run:

```
> info("ethylene", "gas")

info: 2584 refers to ethylene, C2H4 gas (Sho93, 22.Sep.93)
```

`info()` itself is used by other functions in the package. It prints output to the screen, but also returns a numeric value if it finds a species matching the search term. So, we can retrieve the properties of aqueous acetic acid without having to futz with the species ID number.

```
> aadata <- info(info("acetic acid"))

info: acetic acid (C2H4O2) available in aq, liq.
info: 515 refers to acetic acid, C2H4O2 aq (Sho95, 6.Mar.92)

> print(aadata)

           name abbrv formula state source1 source2     date      G       H    S    Cp
515 acetic acid  <NA>  C2H4O2    aq   Sho95    <NA> 6.Mar.92 -94760 -116100 42.7 40.56
        V      a1    a2     a3     a4     c1     c2  omega Z
515 52.01 1.16198 521.8 2.5088 -29946 42.076 -15417 -15000 0
```

4.2 thermo$source

All the thermodynamic and other data, as well as system definitions provided by the user in an interactive session, are stored in an object called `thermo`.

```
> summary(thermo)

         Length Class      Mode
opt      14     -none-     list
element   6     data.frame list
obigt    20     data.frame list
source    2     data.frame list
buffer    4     data.frame list
protein  25     data.frame list
stress   65     data.frame list
groups   22     data.frame list
basis     0     -none-     NULL
species   0     -none-     NULL
water     0     -none-     NULL
water2    0     -none-     NULL
ECO      25     data.frame list
SGD      22     data.frame list
HUM      25     data.frame list
yeastgfp 28     data.frame list
```

The thermodynamic database is stored in a dataframe (an R object that is basically a two-dimensional matrix with named columns) called `thermo$obigt`, and the literature sources of thermodynamic data are listed in `thermo$source`. Most (all?) of the authors who are responsible for these data would be highly grateful if you cite them whenever these data are used in publications.

```
> ts <- thermo$source
> ts[ts$source == aadata$source1, ]

   source                            reference
93  Sho95 E. L. Shock, AJS 295, 496-580, 1995
```

4.3 info() part II

Want to know what acids are in the database?

```
> info("acid")
```

```
info: no match for acid.
info: similar species names, abbreviations, or formulas are:
 [1] "a-aminobutyric acid"     "formic acid"              "acetic acid"
 [4] "propanoic acid"          "n-butanoic acid"          "n-pentanoic acid"
 [7] "n-hexanoic acid"         "n-heptanoic acid"         "n-octanoic acid"
[10] "n-nonanoic acid"         "n-decanoic acid"          "n-undecanoic acid"
[13] "n-dodecanoic acid"       "n-benzoic acid"           "o-toluic acid"
[16] "m-toluic acid"           "p-toluic acid"            "oxalic acid"
[19] "malonic acid"            "succinic acid"            "glutaric acid"
[22] "adipic acid"             "pimelic acid"             "suberic acid"
[25] "azelaic acid"            "sebacic acid"             "glycolic acid"
[28] "lactic acid"             "2-hydroxybutanoic acid"   "2-hydroxypentanoic acid"
[31] "2-hydroxyhexanoic acid"  "2-hydroxyheptanoic acid"  "2-hydroxyoctanoic acid"
[34] "2-hydroxynonanoic acid"  "2-hydroxydecanoic acid"   "aspartic acid"
[37] "glutamic acid"           "uracil"                   "citric acid"
[40] "metacinnabar"            "sanidine,high"            "phosphoric acid"
[43] "acetamide"               "nicotinamide,red"         "nicotinamide,ox"
[46] "n-tridecanoic acid"      "n-tetradecanoic acid"     "n-pentadecanoic acid"
[49] "n-hexadecanoic acid"     "n-heptadecanoic acid"     "n-octadecanoic acid"
[52] "n-nonadecanoic acid"     "n-eicosanoic acid"        "hydrofluoric acid"
[55] "NicotinamideRed"         "NicotinamideOx"
```

That's right, if `info()` can't find an exact match to a name, it does a fuzzy search. That's why "uracil" and "metacinnabar" show up above. If you really just want species whose names include the term "acid", you can add a placeholder character to narrow the search. (Note: don't use an underscore ("_") here because that character is reserved for names of proteins. Any other character will do; here we use a space.)

```
> info(" acid")
```

```
info: no match for  acid.
info: similar species names, abbreviations, or formulas are:
 [1] "a-aminobutyric acid"     "formic acid"              "acetic acid"
 [4] "propanoic acid"          "n-butanoic acid"          "n-pentanoic acid"
 [7] "n-hexanoic acid"         "n-heptanoic acid"         "n-octanoic acid"
[10] "n-nonanoic acid"         "n-decanoic acid"          "n-undecanoic acid"
[13] "n-dodecanoic acid"       "n-benzoic acid"           "o-toluic acid"
[16] "m-toluic acid"           "p-toluic acid"            "oxalic acid"
[19] "malonic acid"            "succinic acid"            "glutaric acid"
[22] "adipic acid"             "pimelic acid"             "suberic acid"
[25] "azelaic acid"            "sebacic acid"             "glycolic acid"
[28] "lactic acid"             "2-hydroxybutanoic acid"   "2-hydroxypentanoic acid"
[31] "2-hydroxyhexanoic acid"  "2-hydroxyheptanoic acid"  "2-hydroxyoctanoic acid"
[34] "2-hydroxynonanoic acid"  "2-hydroxydecanoic acid"   "aspartic acid"
[37] "glutamic acid"           "citric acid"              "phosphoric acid"
[40] "n-tridecanoic acid"      "n-tetradecanoic acid"     "n-pentadecanoic acid"
[43] "n-hexadecanoic acid"     "n-heptadecanoic acid"     "n-octadecanoic acid"
[46] "n-nonadecanoic acid"     "n-eicosanoic acid"        "hydrofluoric acid"
```

The names of species other than proteins use (almost) exclusively lowercase letters. `info()` can also be used to search the text of the chemical formulas as they are entered in the database; the symbols for the elements always start with a capital letter. The example below lists the formulas of aqueous species, then minerals, that contain the symbol commonly used to represent the hydroxide group.

```
> info("(OH)")

info: no match for (OH).
info: similar species names, abbreviations, or formulas are:
 [1] "B(OH)3"                          "U(OH)+3"
 [3] "Ti(OH)4"                         "Pd(OH)2"
 [5] "U(OH)+2"                         "Ru(OH)+"
 [7] "Ru(OH)+2"                        "Rh(OH)+"
 [9] "Rh(OH)+2"                        "Pd(OH)+"
[11] "Pt(OH)+"                         "KAl3(OH)6(SO4)2"
[13] "Mg4Al2(Al2Si2)O10(OH)8"          "Mg2Al(AlSi)O5(OH)4"
[15] "KFe3(AlSi3)O10(OH)2"             "Mg7Si8O22(OH)2"
[17] "Mg48Si34O85(OH)62"               "Mg2(OH)2(CO3)*3H2O"
[19] "Cu3(OH)2(CO3)2"                  "AlO(OH)"
[21] "Mg(OH)2"                         "K(MgAl)Si4O10(OH)2"
[23] "FeAl2SiO5(OH)2"                  "Mg3Si2O5(OH)4"
[25] "Mg5Al(AlSi3)O10(OH)8"            "Ca2Al3Si3O12(OH)"
[27] "Fe2Fe(FeSi)O5(OH)4"              "Fe5Al(AlSi3)O10(OH)8"
[29] "Al2Si2O5(OH)4"                   "Na(Ca2Mg5)(AlSi7)O22(OH2)"
[31] "Ca2FeAl2Si3O12(OH)"              "Na(Ca2Fe5)(AlSi7)O22(OH)2"
[33] "(Fe5Al2)(Al2Si6)O22(OH)2"        "Na(Ca2Fe4Al)(Al2Si6)O22(OH)2"
[35] "(Ca2Fe5)Si8O22(OH)2"             "Al(OH)3"
[37] "Na2(Mg3Al2)Si8O22(OH)2"          "Fe3Si2O5(OH)4"
[39] "Fe7Si8O22(OH)2"                  "Na(Ca2Fe4Fe)(Al2Si6)O22(OH)2"
[41] "Mg5(OH)2(CO3)4*4H2O"             "CaAl2Si2O7(OH)2*H2O"
[43] "Na(Ca2Mg4Fe)(Al2Si6)O22(OH)2"    "Na2(Mg3Fe2)Si8O22(OH)2"
[45] "Cu2(OH)2(CO3)"                   "CaAl2(Al2Si2)O10(OH)2"
[47] "Fe3Si4O10(OH)2"                  "KAl2(AlSi3)O10(OH)2"
[49] "NaAl2(AlSi3)O10(OH)2"            "Na(Ca2Mg4Al)(Al2Si6)O22(OH)2"
[51] "KFe3(AlSi3)O10(OH)O-"            "KMg3(AlSi3)O10(OH)2"
[53] "Ca2Al2Si3O10(OH)2"               "Al2Si4O10(OH)2"
[55] "Na2(CaMg5)Si8O22(OH)2"           "Na2(Fe3Fe2)Si8O22(OH)2"
[57] "Mg4Si6O15(OH)2(H2O)2*4H2O"       "Fe2Al9Si4O23(OH)"
[59] "Mg3Si4O10(OH)2"                  "(Ca2Mg5)Si8O22(OH)2"
[61] "C2H4(OH)2"                       "C3H5(OH)3"
```

5 Proteins

5.1 protein()

There are few things more fun than calculating the standard molal Gibbs energy of formation from the elements at 25 °C and 1 bar of a protein using group additivity. And there are few proteins whose thermodynamic properties more well studied than lysozyme from the egg of the chicken.

```
> protein("LYSC_CHICK")

  protein organism source  abbrv chains Ala Cys Asp Glu Phe Gly His Ile Lys Leu Met Asn
6    LYSC    CHICK BBA+03 P00698      1  12   8   7   2   3  12   1   6   6   8   2  14
  Pro Gln Arg Ser Thr Val Trp Tyr
6   2   3  11  10   7   6   6   3

> protein(6)

protein: found LYSC_CHICK (C613H959N193O185S10, 129 residues)
        name abbrv             formula state source1 source2 date        G         H
```

```
1 LYSC_CHICK    NA C613H959N193O185S10    aq  BBA+03      NA   NA -4206050 -10369700
        S       Cp        V      a1     a2     a3     a4     c1     c2 omega Z
1 4175.86 6415.553 10420.89 2512.58 345.88 450.87 -409.5 7768.7 -701.5 -7.94 0
```

What happened there? Well, the first line extracted the row (rownumber 6) of `thermo$protein` that contains the amino acid composition of LYSC_CHICK. The second line used group additivity [4] to calculate the standard molal thermodynamic properties and equations of state parameters of the protein.

5.2 info()

Most of the time you probably won't be using the `protein()` function. That's because `info()` recognizes the underscore character as being an essential part of the name of a protein. This naming convention is consistent with the Swiss-Prot/UniProtKB naming conventions.

```
> info("LYSC_CHICK")

protein: found LYSC_CHICK (C613H959N193O185S10, 129 residues)
info: 2812 refers to LYSC_CHICK, C613H959N193O185S10 aq (BBA+03)

> info(2812)

           name abbrv             formula state source1 source2 date        G         H
2812 LYSC_CHICK  <NA> C613H959N193O185S10    aq  BBA+03    <NA> <NA> -4206050 -10369700
           S       Cp        V      a1    a2     a3       a4     c1       c2   omega Z
2812 4175.86 6415.553 10420.89 251.258 34588 450.87 -4095000 7768.7 -7015000 -794000 0
```

When CHNOSZ is first loaded, the thermodynamic properties and parameters of the proteins are not present in `thermo$obigt`. In fact, the first call to `info()` just above had a side effect of adding the computed properties and parameters to `thermo$obigt`.

6 Reaction properties

6.1 A single species

A major feature of CHNOSZ is the ability to calculate standard molal properties of species and reactions as a function of temperature and pressure. The function used is called `subcrt()`, which takes its name (with modification) from the well known SUPCRT package [5]. `subcrt()`, like `info()`, takes the name of a species (including proteins) as its first argument (it also works if you give it the numeric index of the species in the database). If no reaction coefficients are given, the function calculates the standard molal properties of the indicated species.

```
> subcrt("water")

subcrt: 1 species at 15 values of T and P (wet)
$species
   name formula state ispecies
1 water     H2O   liq        1

$out
$out$water
        T          P       rho     logK         G         H        S        V       Cp
1    0.01   1.000000 0.9998289 45.03529 -56289.50 -68767.75 15.13238 18.01828 18.20559
2   25.00   1.000000 0.9970614 41.55247 -56687.71 -68316.76 16.71228 18.06830 18.01160
3   50.00   1.000000 0.9880295 38.63281 -57123.89 -67866.54 18.16234 18.23346 18.00464
4   75.00   1.000000 0.9748643 36.15435 -57594.93 -67416.13 19.50485 18.47970 18.04163
5  100.00   1.013220 0.9583926 34.02698 -58098.40 -66963.78 20.75956 18.79731 18.15793
```

```
6  125.00   2.320144 0.9390726 32.18315 -58631.71 -66507.34 21.94192 19.18403 18.33334
7  150.00   4.757169 0.9170577 30.57178 -59193.26 -66045.55 23.06398 19.64456 18.56643
8  175.00   8.918049 0.8923427 29.15313 -59781.38 -65576.63 24.13602 20.18866 18.88296
9  200.00  15.536499 0.8647434 27.89596 -60394.50 -65097.99 25.16818 20.83300 19.32884
10 225.00  25.478603 0.8338733 26.77533 -61031.25 -64605.89 26.17117 21.60424 19.97039
11 250.00  39.736493 0.7990719 25.77115 -61690.35 -64095.00 27.15694 22.54515 20.91232
12 275.00  59.431251 0.7592362 24.86701 -62370.65 -63557.52 28.14000 23.72806 22.35126
13 300.00  85.837843 0.7124075 24.04945 -63071.13 -62980.94 29.14072 25.28777 24.73943
14 325.00 120.457572 0.6545772 23.30725 -63790.84 -62341.39 30.19520 27.52189 29.44748
15 350.00 165.211289 0.5746875 22.63103 -64528.89 -61575.58 31.39713 31.34782 43.59852
```

The columns in the output are temperature (°C), pressure (bar), density of water (g cm^{-3}), logarithm of the equilibrium constant (only meaningful for reactions; see below), and standard molal Gibbs energy and enthalpy of formation from the elements (cal mol^{-1}), and standard molal entropy (cal K^{-1} mol^{-1}), volume (cm^3 mol^{-1}) and heat capacity (cal K^{-1} mol^{-1}).

Compared to other species available in CHNOSZ, liquid H_2O is a weird one, and actually has a dedicated function for calculating its properties. By default, this function calls a Fortran subroutine taken from SUPCRT. Use `help(water)` for more information.

6.2 A reaction

To calculate the properties of a reaction, enter the reaction coefficients as a second argument to `subcrt()`. The function also allows the specification of temperature.

```
> subcrt(c("C2H5OH", "O2", "CO2", "H2O"), c(-1, -3, 2, 3), T = 37)

subcrt: 4 species at 310.15 K and 1 bar (wet)
$reaction
     coeff    name formula state ispecies
112     -1 ethanol  C2H5OH    aq      112
2577    -3  oxygen      O2   gas     2577
69       2     CO2     CO2    aq       69
1        3   water     H2O   liq        1

$out
   T P      rho     logK         G         H         S        V      Cp
1 37 1 0.993325 218.6729 -310330.2 -333262.2 -73.89356 67.43932 67.1269
```

For historical reasons (i.e., the prevalence of the use of oxygen fugacity in geochemical calculations [1]), O_2 breaks the general rule in CHNOSZ that species whose states are not specified are given the aqueous designation if it is available in the thermodynamic database. If you want to specify the physical states of the species in the reaction, that's possible too. For example, we can ensure that dissolved O_2 is used in the calculation instead of the gaseous form.

```
> subcrt(c("C2H5OH", "O2", "CO2", "H2O"), c(-1, -3, 2, 3), c("liq", "aq",
+     "aq", "liq"), T = 37)

subcrt: 4 species at 310.15 K and 1 bar (wet)
$reaction
     coeff    name formula state ispecies
2373    -1 ethanol  C2H5OH   liq     2373
67      -3      O2      O2    aq       67
69       2     CO2     CO2    aq       69
1        3   water     H2O   liq        1

$out
```

```
   T P      rho     logK         G       H         S         V        Cp
1 37 1 0.993325 229.2001 -325269.9 -328765 -11.35425 -30.47709 -32.18662
```

A useful feature of `subcrt()` is that it emits a warning if the reaction is not balanced. Let's say you forgot to account for oxygen on the left-hand side of the reaction (similar to the reaction found at the Wikipedia entry on ethanol metabolism on 2010-09-23: "Complete Reaction: C_2H_6O(Ethanol)→C_2H_4O(Acetaldehyde)→$C_2H_4O_2$(acetic Acid) →Acetyl-CoA→$3H_2O$+$2CO_2$").

```
> subcrt(c("C2H5OH", "CO2", "H2O"), c(-1, 2, 3), T = 37)

subcrt: 3 species at 310.15 K and 1 bar (wet)
subcrt: reaction is not balanced; it is missing this composition:
  O
 -6
$reaction
    coeff    name formula state ispecies
112    -1 ethanol  C2H5OH    aq      112
69      2     CO2     CO2    aq       69
1       3   water     H2O   liq        1

$out
   T P      rho     logK         G         H        S        V       Cp
1 37 1 0.993325 219.9202 -312100.3 -333009.0 74.02581 67.43932 88.28986
```

In the next section we'll see how to use another feature of CHNOSZ to automatically balance reactions.

7 Basis species

7.1 What are basis species?

Basis species are a minimal set of chemical species that represent the compositional variation in a system. system Operationally, a **system** is the combination of basis species and species of interest which is set up by the user to investigate a real-life system. The basis species are akin to thermodynamic components, but can include charged species.

There are at least two reasons to define the basis species when using CHNOSZ. First, you might want to use them to automatically balance reactions. Second, they are required for making chemical activity diagrams. Let's start with an example that *doesn't* work.

```
> basis(c("CO2", "H2O", "NH3", "H2S", "H+"))


    Error in put.basis(basis, mystates) :
      this is not a valid stoichiometric matrix.
    In addition: Warning messages:
    1: basis: 5 compounds ( CO2 H2O NH3 H2S H+ )
    2: basis: 6 elements ( C H N O S Z )
```

CHNOSZ requires that there be one basis species for each different element, and charge if present. Why? So that any possible species of interest that contains these elements can be represented by a linear combination of the basis species. Now let's make a working basis definition.

```
> basis(c("CO2", "H2O", "NH3", "O2", "H2S", "H+"))
```

```
    C H N O S Z ispecies logact state
CO2 1 0 0 2 0 0       69      0    aq
H2O 0 2 0 1 0 0        1      0   liq
NH3 0 3 1 0 0 0       68      0    aq
O2  0 0 0 2 0 0     2577      0   gas
H2S 0 2 0 0 1 0       70      0    aq
H+  0 1 0 0 0 1        3      0    aq
```

Awesome. First basis definition! Note the column names, which give CHNOSZ its name. These represent the major elements in the common amino acids, together with Z, which stands for charge.

7.2 Auto-balancing a reaction

Now that the basis species are defined, try the unbalanced reaction again.

```
> subcrt(c("C2H5OH", "CO2", "H2O"), c(-1, 2, 3), T = 37)

subcrt: 3 species at 310.15 K and 1 bar (wet)
subcrt: reaction is not balanced; it is missing this composition:
  O
 -6
subcrt: adding missing composition from basis definition and restarting...
subcrt: 4 species at 310.15 K and 1 bar (wet)
$reaction
     coeff    name formula state ispecies
112     -1 ethanol  C2H5OH    aq      112
69       2     CO2     CO2    aq       69
1        3   water     H2O   liq        1
2577    -3  oxygen      O2   gas     2577

$out
   T P     logK         G         H         S        V      Cp
1 37 1 218.6729 -310330.2 -333262.2 -73.89356 67.43932 67.1269
```

Cool! `subcrt()` detected an unbalanced reaction, but since the missing element was among the elements of the basis species, it added the appropriate amount of $O_{2(gas)}$ to the reaction before running the calculations. You can go even further and eliminate CO_2 and H_2O from the function call, but still get the same results.

```
> subcrt(c("C2H5OH"), c(-1), T = 37)

subcrt: 1 species at 310.15 K and 1 bar (wet)
subcrt: reaction is not balanced; it is missing this composition:
 C H O
 2 6 1
subcrt: adding missing composition from basis definition and restarting...
subcrt: 4 species at 310.15 K and 1 bar (wet)
$reaction
     coeff    name formula state ispecies
112     -1 ethanol  C2H5OH    aq      112
69       2     CO2     CO2    aq       69
1        3   water     H2O   liq        1
2577    -3  oxygen      O2   gas     2577

$out
   T P     logK         G         H         S        V      Cp
1 37 1 218.6729 -310330.2 -333262.2 -73.89356 67.43932 67.1269
```

What if you were interested in the thermodynamic properties of the reaction of ethanol to acetaldehyde, but didn't want to balance the reaction yourself (and you also didn't know how the formulas of the species are written in the database)?

```
> subcrt(c("ethanol", "acetaldehyde"), c(-1, 1), T = 37)

subcrt: 2 species at 310.15 K and 1 bar (wet)
subcrt: reaction is not balanced; it is missing this composition:
 H
 2
subcrt: adding missing composition from basis definition and restarting...
subcrt: 4 species at 310.15 K and 1 bar (wet)
$reaction
     coeff         name formula state ispecies
112   -1.0      ethanol  C2H5OH    aq      112
256    1.0 acetaldehyde  CH3CHO    aq      256
1      1.0        water     H2O   liq        1
2577  -0.5       oxygen      O2   gas     2577

$out
   T P     logK         G        H         S        V        Cp
1 37 1 32.90437 -46696.31 -50194.4 -11.18783 7.708236 -11.86250
```

Notice how 2 H's needed to be added to the right-hand side of the reaction, which is the equivalent of $H_2O - 0.5O_2$. With a different choice of basis species, but the same elements, the reaction might look quite different. As an extreme example, suppose you had amino acids in mind. The first line below, `data(thermo)`, is a quick way to reset the thermo object to its original state, in other words to forget the current system definition.

```
> data(thermo)

thermo$obigt has 1782 aqueous, 2811 total species

> basis(c("glycine", "alanine", "lysine", "glutamic acid", "cysteine",
+     "H+"))

          C  H N O S Z ispecies logact state
C2H5NO2   2  5 1 2 0 0     1516      0    aq
C3H7NO2   3  7 1 2 0 0     1504      0    aq
C6H14N2O2 6 14 2 2 0 0     1522      0    aq
C5H9NO4   5  9 1 4 0 0     1514      0    aq
C3H7NO2S  3  7 1 2 1 0     1511      0    aq
H+        0  1 0 0 0 1        3      0    aq

> subcrt(c("ethanol", "acetaldehyde"), c(-1, 1), T = 37)

subcrt: 2 species at 310.15 K and 1 bar (wet)
subcrt: reaction is not balanced; it is missing this composition:
 H
 2
subcrt: adding missing composition from basis definition and restarting...
subcrt: 6 species at 310.15 K and 1 bar (wet)
$reaction
     coeff          name   formula state ispecies
112     -1       ethanol    C2H5OH    aq      112
256      1  acetaldehyde    CH3CHO    aq      256
```

```
1516    -2       glycine   C2H5NO2    aq     1516
1504     5       alanine   C3H7NO2    aq     1504
1522    -1        lysine C6H14N2O2    aq     1522
1514    -1 glutamic acid   C5H9NO4    aq     1514

$out
   T P      logK        G         H         S        V       Cp
1 37 1 -1.066685 1513.789 -345.4114 -5.865828 5.832194 14.27545
```

In this case, the function finds that 2 H's are the equivalent of $-2C_2H_5NO_2 + 5C_3H_7NO_2 - C_6H_{14}N_2O_2 - C_5H_9NO_4$. It's pretty easy for the computer to figure that out using basic matrix operations, but not likely something you'd want to do by hand. You might complain that this reaction is not likely to represent an actual metabolic process ... as always, the challenge (and fun) of coming up with a useful basis definition is in relating them to observable quantities.

7.3 It works for proteins too!

As noted above, `subcrt()` can take the name of a protein as an argument.

```
> data(thermo)

thermo$obigt has 1782 aqueous, 2811 total species

> basis("CHNOS+")

    C H N O S Z ispecies logact state
CO2 1 0 0 2 0 0       69     -3    aq
H2O 0 2 0 1 0 0        1      0   liq
NH3 0 3 1 0 0 0       68     -4    aq
H2S 0 2 0 0 1 0       70     -7    aq
O2  0 0 0 2 0 0     2577    -80   gas
H+  0 1 0 0 0 1        3     -7    aq

> subcrt("LYSC_CHICK", 1, T = 25)

protein: found LYSC_CHICK (C613H959N193O185S10, 129 residues)
subcrt: 1 species at 298.15 K and 1 bar (wet)
subcrt: reaction is not balanced; it is missing this composition:
    C    H    N    O   S
 -613 -959 -193 -185 -10
subcrt: adding missing composition from basis definition and restarting...
subcrt: 6 species at 298.15 K and 1 bar (wet)
$reaction
      coeff       name             formula state ispecies
2812    1.0 LYSC_CHICK C613H959N193O185S10    aq     2812
69   -613.0        CO2                CO2    aq       69
1    -180.0      water                H2O   liq        1
68   -193.0        NH3                NH3    aq       68
70    -10.0        H2S                H2S    aq       70
2577  610.5     oxygen                 O2   gas     2577

$out
   T P      logK        G        H        S         V        Cp
1 25 1 -46799.28 63845637 66394946 8600.944 -18320.13 -27314.51
```

The reaction properties for proteins are quite large compared to the reactions with ethanol. If the name of the protein is not found in CHNOSZ's own database, the protein sequence can be retrieved from the Swiss-Prot database (if the computer is connected to the internet)

```
> subcrt("ALAT1_HUMAN", 1, T = 25)
```

For the basis definition we used a keyword that refers to a preset combination of commonly used basis species. Note that this also sets the logarithms of activities (fugacity in the case of $O_{2(g)}$) to reference values. While these values do not affect the results of the `subcrt()` calculation (which normally returns only the standard molal properties of the reaction), they are essential in calculating the relative stabilities of the species of interest.

8 Activity diagrams

8.1 Quick example: stability diagram for proteins

Now we're going to get into the heart of CHNOSZ: the `affinity()` function. First we start by defining the basis species.

```
> basis("CHNOS+")
```

```
    C H N O S Z ispecies logact state
CO2 1 0 0 2 0 0       69     -3    aq
H2O 0 2 0 1 0 0        1      0   liq
NH3 0 3 1 0 0 0       68     -4    aq
H2S 0 2 0 0 1 0       70     -7    aq
O2  0 0 0 2 0 0     2577    -80   gas
H+  0 1 0 0 0 1        3     -7    aq
```

Then we define the **species of interest**, i.e. those whose relative stabilities we wish to calculate. We will use part of a case study presented in Ref. [3]. *Methanocaldococcus jannaschii* is a hyperthermophilic methanogen known to live at higher temperatures than *Methanococcus voltae* (also a methanogen) and *Haloarcula japonica* (a halophile). These archaeal organisms produce cell-surface glycoproteins (a.k.a. surface-layer proteins).

```
> species(c("CSG_METJA", "CSG_METVO", "CSG_HALJP"))
```

```
protein: found CSG_METJA (C2555H4032N640O865S14, 530 residues)
protein: found CSG_METVO (C2575H4097N645O884S11, 553 residues)
protein: found CSG_HALJP (C3669H5647N971O1488, 828 residues)
   CO2  H2O NH3 H2S      O2 H+ ispecies logact state      name
1 2555 1042 640  14 -2643.5  0     2813     -3    aq CSG_METJA
2 2575 1070 645  11 -2668.0  0     2814     -3    aq CSG_METVO
3 3669 1367 971   0 -3608.5  0     2815     -3    aq CSG_HALJP
```

Note the output: the matrix denotes the coefficients of each of the basis species in the formation reaction for one mole of each of the species of interest. The **formation reaction** is the chemical reaction to form (as a product) one mole of a species of interest from a combination of basis species (as reactants and/or products, depending on the stoichiometry). The species definition also includes reference values for the chemical activities of the species of interest.

Now we are all set up to calculate the chemical affinities of the formation reactions. The chemical affinity is the negative of the Gibbs energy change per unit of reaction progress of a reaction; it is calculated in CHNOSZ using $\boldsymbol{A} = 2.303RT\log(K/Q)$ (R – gas constant, T – temperature, K – equilibrium constant, Q – activity product).

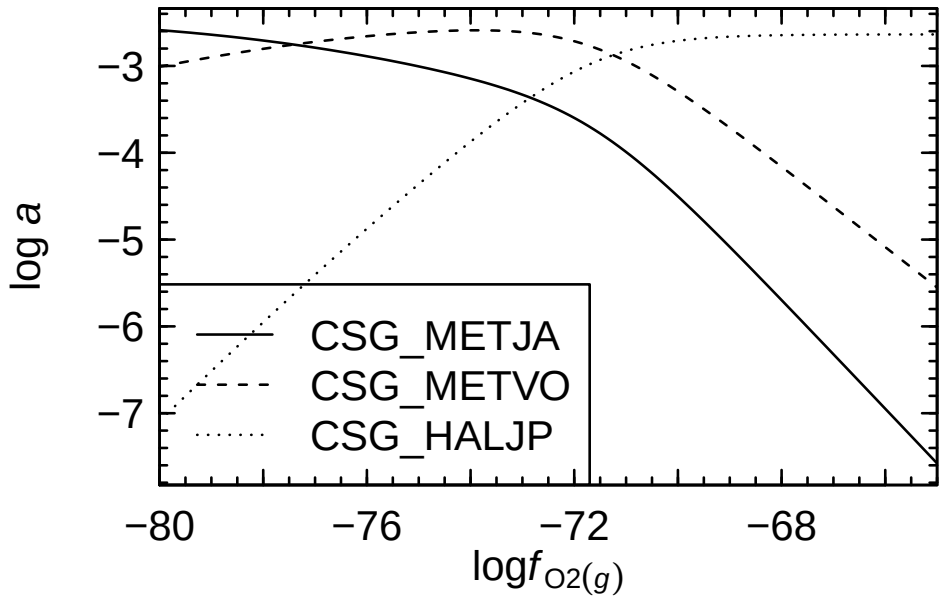
`affinity()` is a versatile function that accepts any number of arguments describing the range of chemical conditions we're interested in. Here, we choose to vary the logarithm of the fugacity of oxygen from −90 to −65. The chemical activities of the other basis species are taken to be constants equal to the values shown above after the call to `basis()`.

```
> a <- affinity(O2 = c(-80, -65))
```

```
affinity: temperature is 25 C
energy.args: pressure is Psat
energy.args: variable 1 is O2 at 128 increments from -80 to -65
affinity: loading ionizable protein groups
subcrt: 26 species at 298.15 K and 1 bar (wet)
```

Finally, we can use `diagram()` to plot the relative stabilities of the proteins in the system. We'll also specify where the legend should be placed on the plot.

```
> diagram(a, legend.x = "bottomleft")

diagram: immobile component is protein backbone group
diagram: conservation coefficients are 530 553 828
diagram: using residue equivalents
diagram: log total activity of PBB (from species) is 0.2812607
```



Notably, the protein from the hyperthermophilic organism is relatively stable at lower oxidation states.

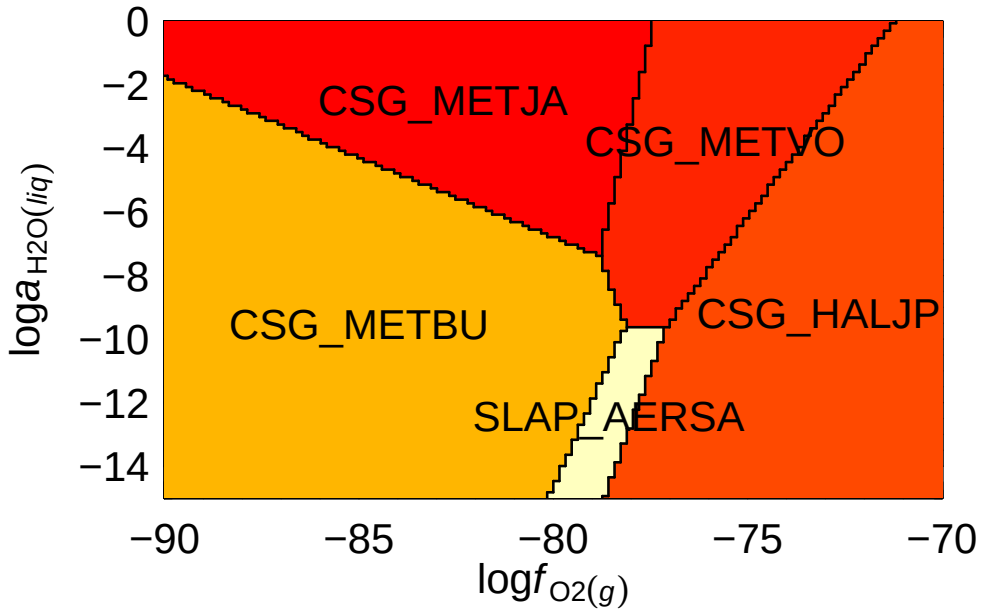
8.2 Why does this work?

Here is a partial explanation: You use `affinity()` to calculate the chemical affinities of the formation reactions of the proteins, taking into account chemical activities of the proteins that are set to reference, non-equilibrium values. Then, the `diagram()` function transforms these non-equilibrium affinities into chemical activities of the proteins at metastable equilibrium (this is actually achieved using the Maxwell-Boltzmann distribution). These activities satisfy the conditions that 1) the total activity of a conserved component (for proteins, this is usually the protein backbone group) is constant and 2) the chemical affinities of the formation reactions are all equal (but not zero).

8.3 More proteins, more dimensions

Let's get more proteins into the act.

```
> species(c("CSG_METSC", "CSG_METFE", "CSG_METBU"))

protein: found CSG_METSC (C2812H4405N747O872S16, 571 residues)
protein: found CSG_METFE (C2815H4411N747O872S14, 571 residues)
protein: found CSG_METBU (C1362H2111N355O442S4, 278 residues)
   CO2  H2O NH3 H2S      O2 H+ ispecies logact state      name
1 2555 1042 640  14 -2643.5  0     2813     -3    aq CSG_METJA
2 2575 1070 645  11 -2668.0  0     2814     -3    aq CSG_METVO
3 3669 1367 971   0 -3608.5  0     2815     -3    aq CSG_HALJP
4 2812 1066 747  16 -2909.0  0     2816     -3    aq CSG_METSC
5 2815 1071 747  14 -2914.5  0     2817     -3    aq CSG_METFE
6 1362  519 355   4 -1400.5  0     2818     -3    aq CSG_METBU

> species(c("SLAP_ACEKI", "SLAP_BACST", "SLAP_BACLI", "SLAP_AERSA"))

protein: found SLAP_ACEKI (C3584H5648N926O1138S4, 736 residues)
protein: found SLAP_BACST (C5676H9113N1489O1863S3, 1198 residues)
protein: found SLAP_BACLI (C3977H6396N1068O1286S2, 844 residues)
protein: found SLAP_AERSA (C2250H3580N618O716S2, 481 residues)
    CO2  H2O  NH3 H2S      O2 H+ ispecies logact state       name
1  2555 1042  640  14 -2643.5  0     2813     -3    aq  CSG_METJA
2  2575 1070  645  11 -2668.0  0     2814     -3    aq  CSG_METVO
3  3669 1367  971   0 -3608.5  0     2815     -3    aq  CSG_HALJP
4  2812 1066  747  16 -2909.0  0     2816     -3    aq  CSG_METSC
5  2815 1071  747  14 -2914.5  0     2817     -3    aq  CSG_METFE
6  1362  519  355   4 -1400.5  0     2818     -3    aq  CSG_METBU
7  3584 1431  926   4 -3730.5  0     2819     -3    aq SLAP_ACEKI
8  5676 2320 1489   3 -5904.5  0     2820     -3    aq SLAP_BACST
9  3977 1594 1068   2 -4131.0  0     2821     -3    aq SLAP_BACLI
10 2250  861  618   2 -2322.5  0     2822     -3    aq SLAP_AERSA

> a <- affinity(O2 = c(-90, -70), H2O = c(-15, 0))

affinity: temperature is 25 C
energy.args: pressure is Psat
energy.args: variable 1 is O2 at 128 increments from -90 to -70
energy.args: variable 2 is H2O at 128 increments from -15 to 0
affinity: loading ionizable protein groups
subcrt: 33 species at 298.15 K and 1 bar (wet)

> diagram(a)

diagram: immobile component is protein backbone group
diagram: conservation coefficients are 530 553 828 571 571 278 736 1198 844 481
diagram: using residue equivalents
```



Stability fields for proteins as a function of two chemical activities! This example hints at the multidimensional nature of the stability problem. By carefully choosing a system for consideration, this type of analysis might be useful in relating the occurrence of proteins and organisms to environmental characteristics. (If you don't like the colors used in the plot, don't worry... the colors can be changed by using additional options to `diagram()`.)

8.4 A mineral example

This example is modeled after a figure on p. 246 of Bowers et al., 1984 [2] for the system HCl-H2O-CaO-CO2-MgO-(SiO2) at 300 °C and 1000 bar.

```
> basis(c("HCl", "H2O", "Ca+2", "CO2", "Mg+2", "SiO2", "O2", "H+"), c(999,
+     0, 999, 999, 999, 999, 999, -7))
```

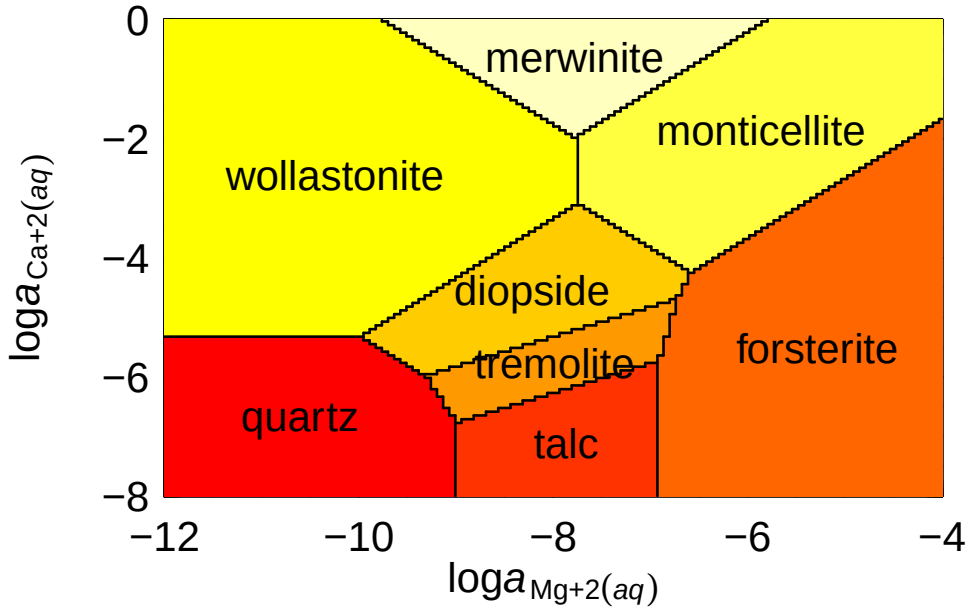
```
     C Ca Cl H Mg O Si Z ispecies logact state
HCl  0  0  1 1  0 0  0 0      883    999    aq
H2O  0  0  0 2  0 1  0 0        1      0   liq
Ca+2 0  1  0 0  0 0  0 2       10    999    aq
CO2  1  0  0 0  0 2  0 0       69    999    aq
Mg+2 0  0  0 0  1 0  0 2        9    999    aq
SiO2 0  0  0 0  0 2  1 0       72    999    aq
O2   0  0  0 0  0 2  0 0     2577    999   gas
H+   0  0  0 1  0 0  0 1        3     -7    aq
```

```
> species(c("quartz", "talc", "forsterite", "tremolite", "diopside", "wollastonite",
+     "monticellite", "merwinite"))
```

```
  HCl H2O Ca+2 CO2 Mg+2 SiO2 O2  H+ ispecies logact state         name
1   0   0    0   0    0    1  0   0     1987      0   cr1       quartz
2   0   4    0   0    3    4  0  -6     2012      0    cr         talc
3   0   2    0   0    2    1  0  -4     1902      0    cr   forsterite
4   0   8    2   0    5    8  0 -14     2014      0    cr    tremolite
```

```
5   0   2    1   0    1    2  0  -4     1873      0    cr     diopside
6   0   1    1   0    0    1  0  -2     2016      0    cr wollastonite
7   0   2    1   0    1    1  0  -4     1958      0    cr monticellite
8   0   4    3   0    1    2  0  -8     1954      0    cr    merwinite
```

```
> a <- affinity(`Mg+2` = c(-12, -4), `Ca+2` = c(-8, 0), T = 300, P = 1000)

affinity: temperature is 300 C
affinity: pressure is 1000 bar
energy.args: variable 1 is Mg+2 at 128 increments from -12 to -4
energy.args: variable 2 is Ca+2 at 128 increments from -8 to 0
subcrt: 16 species at 573.15 K and 1000 bar (wet)

> diagram(a)

     C Ca Cl H Mg O Si Z ispecies logact state
HCl  0  0  1 1  0 0  0 0      883    999    aq
H2O  0  0  0 2  0 1  0 0        1      0   liq
Ca+2 0  1  0 0  0 0  0 2       10    999    aq
CO2  1  0  0 0  0 2  0 0       69    999    aq
Mg+2 0  0  0 0  1 0  0 2        9    999    aq
SiO2 0  0  0 0  0 2  1 0       72    999    aq
O2   0  0  0 0  0 2  0 0     2577    999   gas
H+   0  0  0 1  0 0  0 1        3     -7    aq
diagram: immobile component is SiO2
diagram: conservation coefficients are 1 4 1 8 2 1 1 2
```



There are several particulars to note about the commands. The 999's in the assignment of logarithms of activities of basis species indicate that these values do not affect the outcome of the calculation. This is so because 1) HCl, CO2, O2 have zero stoichiometric coeffs in the species, 2) Ca+2, Mg+2 are variables of interest (and their ranges are taken from the call to `affinity()`), and 3) SiO2 is the conserved (immobile) component. Also note that "Mg+2" and "Ca+2" are not syntactically valid object names, but we can force R

to deal with them by putting them in quotation marks in the call to `affinity()`. The calculation is slightly different from that used in Ref. [2], where the axes are $\log\left(a_{Mg^{+2}}/a_{H^+}^2\right)$ and $\log\left(a_{Ca^{+2}}/a_{H^+}^2\right)$.

In just a few lines it's possible to make a wide variety of activity diagrams for organic and inorganic species. Try it with your favorite system!

9 Where to go from here

You can explore the package documentation through R's help system; just type `help.start()` at the command line and select CHNOSZ in the browser window that comes up. If you want to get an idea of the types of calculations available in CHNOSZ, run the examples in the help files, for example `diagram()`. (For the purposes of this document, the output of the code below is not shown here.)

```
> example(diagram)
```

Or you can use the following to run all of the examples provided in the documentation for the package. You will see a lot of text fly by on the screen, as well as a variety of plots. The examples will take about 10-20 minutes to run, depending on your machine.

```
> examples()
```

If you want to modify the database, first find the location of the data files:

```
> system.file(package = "CHNOSZ")
```

```
[1] "/home/jedick/R/x86_64-slackware-linux-gnu-library/2.12/CHNOSZ"
```

The result will be different on your system. In the `data` directory at that location are comma-separated-value (CSV) files; the one named OBIGT.csv is the primary thermodynamic database. After modifying it, save the file and restart CHNOSZ and your modifications will be visible.

Have fun!

10 Document information

Revision history:

- 2010-09-30 Initial version

R session information:

```
> sessionInfo()
```

```
R version 2.12.1 (2010-12-16)
Platform: x86_64-slackware-linux-gnu (64-bit)

locale:
 [1] LC_CTYPE=en_US       LC_NUMERIC=C         LC_TIME=en_US        LC_COLLATE=C
 [5] LC_MONETARY=C        LC_MESSAGES=en_US    LC_PAPER=en_US       LC_NAME=C
 [9] LC_ADDRESS=C         LC_TELEPHONE=C       LC_MEASUREMENT=en_US LC_IDENTIFICATION=C

attached base packages:
[1] tools     stats     graphics  grDevices utils     datasets  methods   base

other attached packages:
[1] CHNOSZ_0.9-3
```

References

[1] G. M. Anderson. *Thermodynamics of Natural Systems*. Cambridge University Press, 2nd edition, 2005. URL http://www.cambridge.org/0521847729.

[2] T. S. Bowers, K. J. Jackson, and H. C. Helgeson. *Equilibrium Activity Diagrams for Coexisting Minerals and Aqueous Solutions at Pressures and Temperatures to 5 kb and 600° C*. Springer-Verlag, Heidelberg, 1984. URL http://www.worldcat.org/oclc/11133620.

[3] J. M. Dick. Calculation of the relative metastabilities of proteins using the CHNOSZ software package. *Geochem. Trans.*, 9:10, 2008. doi: 10.1186/1467-4866-9-10. URL http://www.geochemicaltransactions.com/content/9/1/10.

[4] J. M. Dick, D. E. LaRowe, and H. C. Helgeson. Temperature, pressure, and electrochemical constraints on protein speciation: Group additivity calculation of the standard molal thermodynamic properties of ionized unfolded proteins. *Biogeosciences*, 3(3):311 – 336, 2006. URL http://www.biogeosciences.net/3/311/2006/.

[5] J. W. Johnson, E. H. Oelkers, and H. C. Helgeson. SUPCRT92: A software package for calculating the standard molal thermodynamic properties of minerals, gases, aqueous species, and reactions from 1 to 5000 bar and 0 to 1000°C. *Comp. Geosci.*, 18(7):899 – 947, 1992. URL http://dx.doi.org/10.1016/0098-3004(92)90029-Q.