Crust to Core workshop: An introduction to Perple_X

Part 2: The structure of a Perple_X calculation

ETH
Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich
Institute of Mineralogy and Petrology

Perple_X:

- Is written and maintained by Jamie Connolly (ETH Zürich)
- Is written in FORTRAN, with the source code available.
- Took quite a long time to write…
- Accepts thermodynamic data from any source, provided it is formatted correctly (in a simple text file).

Connolly, J.A.D., Kerrick, D.M., 1987. An algorithm and computer program for calculating composition phase diagrams. *Computers and Geosciences* **11**, 1-55.

Connolly, J.A.D., 1990. Multivariable phase diagrams: an algorithm based on generalized thermodynamics. *Am. J. Sci.* **290**, 666-718.

Kerrick, D.M., Connolly, J.A.D., 2001. Metamorphic devolatilization of subducted marine sediments and the transport of volatiles into the Earth's mantle. *Nature* **411**, 293-296.

Connolly, J.A.D., Petrini, K., 2002. An automated strategy for calculation of phase diagram sections and retrieval of rock properties as a function of physical conditions. *J. Metamorph. Geol.* **20**, 697-708.

Connolly, J.A.D., 2005. Computation of phase equilibria by linear programming: A tool for geodynamic modeling and its application to subduction zone decarbonation. *Earth Planet. Sci. Lett.* **236**, 524-541.

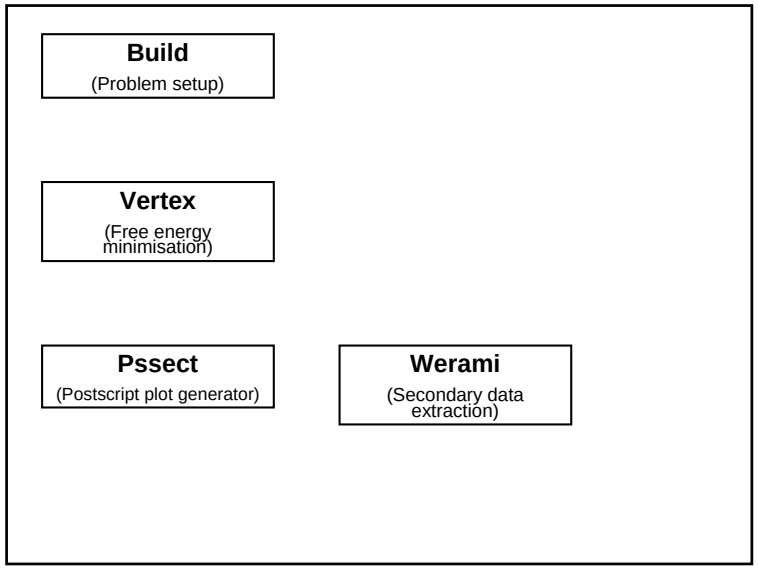
Caddick, M.J., Thompson, A.B., 2008. Quantifying the tectono-metamorphic evolution of pelitic rocks from a wide range of tectonic settings: Mineral compositions in equilibrium. *Contrib. Mineral. Petrol.* **156**, 177-195.

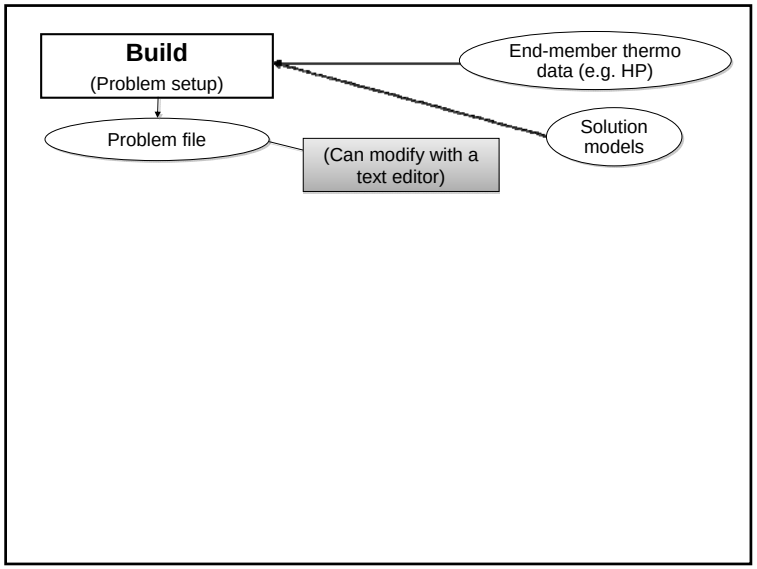
Perple_X:

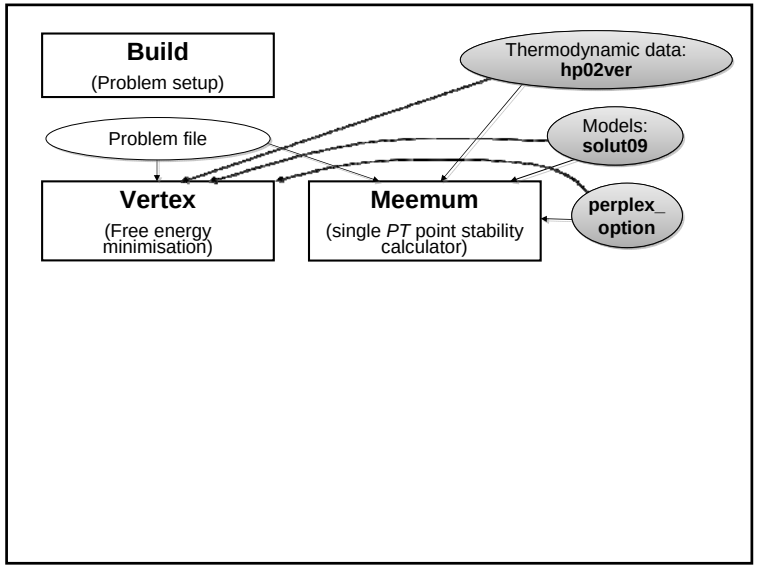
- Minimises free energy of multiple phase configurations to identify the 'most stable' set.
- Can work with complex phases by breaking solution-space into a number of discrete 'phases' (pseudo-compounds).
- Is *very* flexible, generating:
  - *PT* projections
  - Pseudosections
  - Compatability diagrams (e.g. AFM triangles)
  - Mixed-variable diagrams
- Is *very* flexible, allowing:
  - Complex saturation heirarchies
  - Transformation of components
  - Use of numerous EOS for fluids involving H_2O, CO_2, NaCl
  - Easy extraction of sub-systems from large solution model files

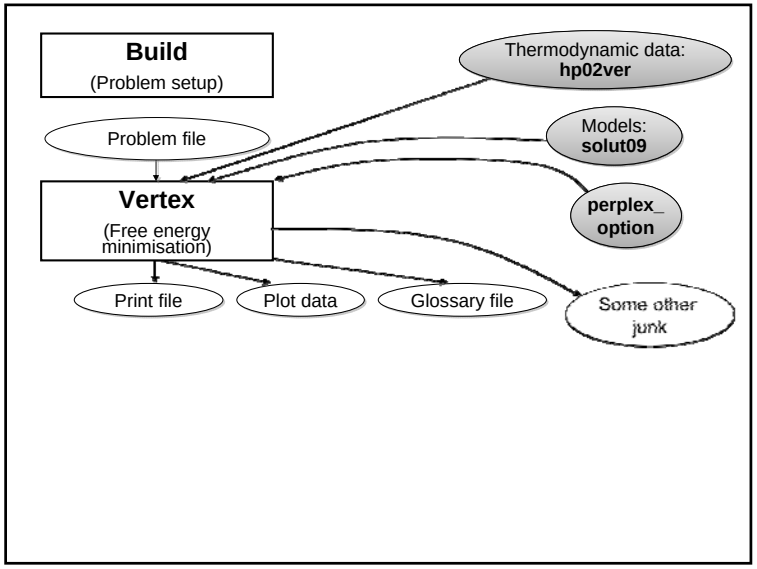
Perple_X:

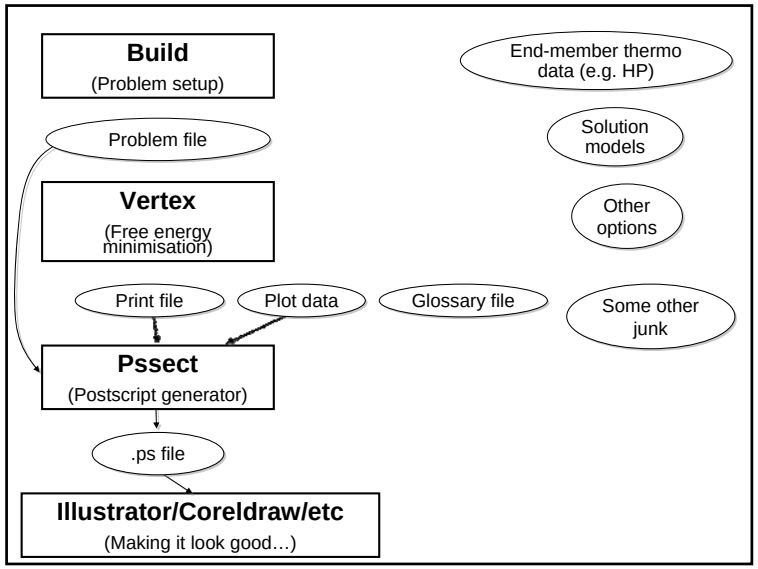
- Permits easy extraction of secondary data:
  - Modes of phases
  - Compositions of phases
  - Phase or bulk-rock density
  - Other phase or bulk-rock properties (heat capacity, enthalpy, bulk modulus)
  - Estimated secondary properties (P- and S-wave velocities)
- Is a modular collection of many (> 10) sub-programs which can generate a bewildering array of files…
- Requires minimal user input.
- Has the ability to confuse at first.
- But is actually incredibly simple to use.
- Is *much* more efficient than it used to be.
- But can still take a *long* time to calculate a diagram.

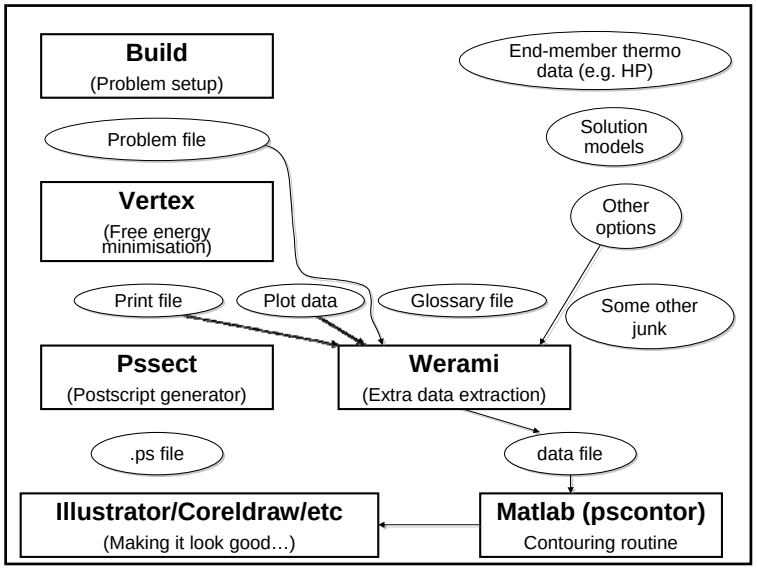

Build
(Problem setup)
Vertex
(Free energy minimisation)
Pssect
(Postscript plot generator)
Werami
(Secondary data extraction)


Build
(Problem setup)
End-member thermo data (e.g. HP)
Solution models
Problem file
(Can modify with a text editor)


Build
(Problem setup)
Thermodynamic data: hp02ver
Problem file
Models: solut09
Vertex
(Free energy minimisation)
Meemum
(single PT point stability calculator)
perplex_ option

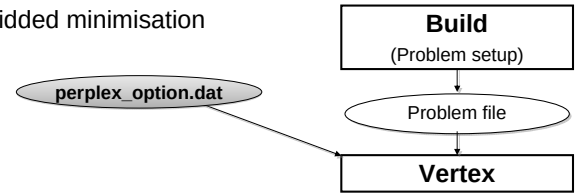

Build
(Problem setup)
Thermodynamic data: hp02ver
Problem file
Models: solut09
Vertex
(Free energy minimisation)
perplex_ option
Print file
Plot data
Glossary file
Some other junk





A better solution requires understanding of:

1. Gridded minimisation

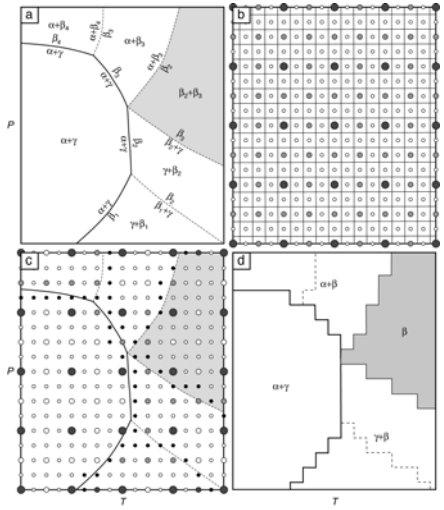


2. Models for phases with solid solutions

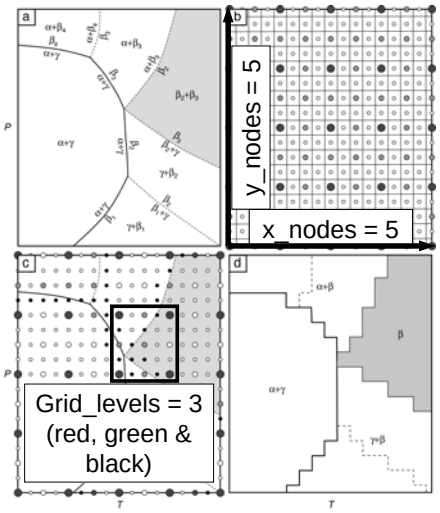
   - The pseudocompound approximation
   - Auto refine & iteration

Controlled by
- Solution models
- Perplex options

Gridded minimisation



Gridded minimisation



In the "*perplex_options.dat*" file:

• *x_nodes* & *y_nodes* define the number of red dots

• *grid_levels* defines the amount of iteration

Solution models for complex phases

Phases of variable composition, (**solution phases**), are invariably described as a mixture of *s* real or hypothetical **endmembers**, for which data is tabulated. The problem is then to formulate a **solution model** that describes the Gibbs energy of such a solution phase in terms of these endmembers. Such models consist of three components $G = G^{mech} + G^{conf} + G^{excess}$ where G^{mech} is the energy arising from mechanically mixing of the endmembers, G^{conf} is the energy expected to arise from theoretical entropic considerations, and G^{excess} is a component that accounts for the energetic effects caused by distortions of the atomic structure (e.g., strain) of the chemical mixing process or, in some cases, simply error in G^{conf}.

(Connolly, 2006)

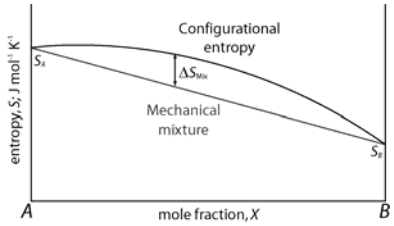
Three main types of solution model:

- **Ideal** (ΔS_{config} considered, ΔG_{excess} not considered)
- **Regular** (ΔS_{config} & ΔG_{excess} considered)
- **Asymmetric** (as above, minima not at $X_i = 0.5$)

Three levels of complexity:

- **Single site** mixing (e.g. Mg - Fe in olivine; Mg, Fe, Ca, Mn mixing in garnet)
- **Multiple site** mixing (e.g. Mg, Fe, Ca, Mn **&** Fe^{3+} -③Al in garnet)
- **Multiple site** mixing requiring **charge balance** (e.g. NaSi ③CaAl in plagioclase feldspar)

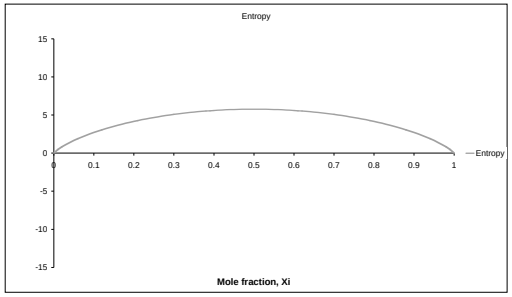
Assuming simple binary mixing e.g. Fe-Mg in garnet



In a simple mechanical mixture, energy varies linearly between the values of the two end-members

In an ideal solid solution, configurational entropy must be considered

Assuming simple binary mixing e.g. Fe-Mg in garnet



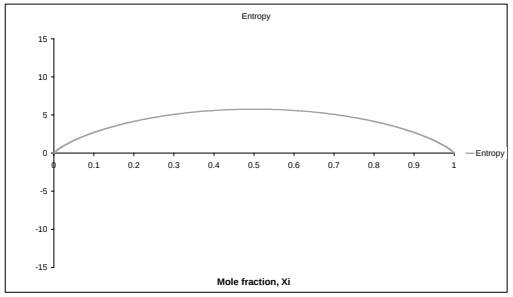
Configurational entropy is a function of disorder, so logically must be at a maximum when the X_i = 0.5. It follows that S_{config} must always be positive.

The general formula for S_{config} in a phase with a single crystallographic site:

$$\bar{S}_{\text{config}} = -\alpha_c \, \mathrm{R} \sum_{i=1}^{n} X_i \ln X_i$$

Where R is the gas constant and α_c is the site multiplicity

Assuming simple binary mixing e.g. Fe-Mg in garnet



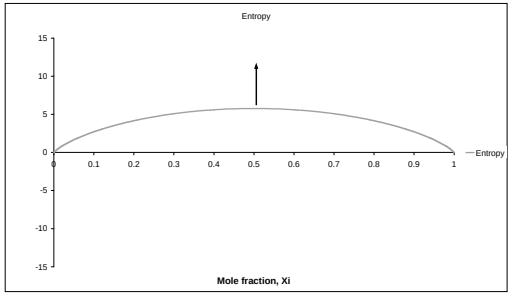
In our binary case:

$$\bar{S}_{\text{Config}} = -\alpha_c \, \mathrm{R} \left(X_A \ln X_A + X_B \ln X_B \right)$$

$$\bar{S}_{\text{Config}} = -\alpha_c \, \mathrm{R} \left(X_i \ln X_i + \left[1 - X_i\right] \ln \left[1 - X_i\right] \right)$$

Where R is the gas constant and α_c is the site multiplicity

Assuming simple binary mixing e.g. Fe-Mg in garnet

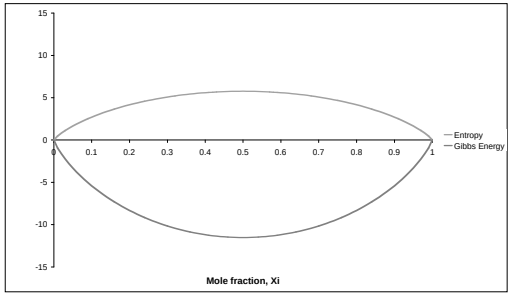


Entropy from multiple site mixing simply requires summing terms, e.g., for a phase with two distinct crystallographic sites:

General formula = $(\mathrm{A},\mathrm{B})_{\alpha}(\mathrm{Y},\mathrm{Z})_{\beta}$

$$\bar{S}_{\text{Config}} = -\mathrm{R} \left(\alpha X_A \ln X_A + \alpha X_B \ln X_B + \beta X_Y \ln X_Y + \beta X_Z \ln X_Z \right)$$

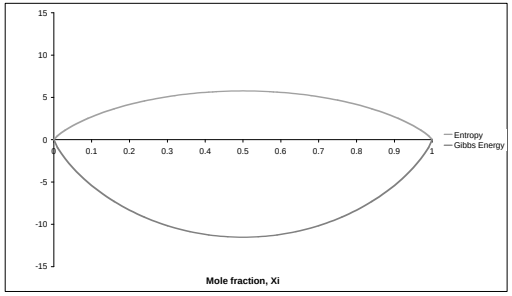
Assuming simple binary mixing e.g. Fe-Mg in garnet



In the ideal case we assume that enthalpy = 0, so $G = -TS$.

So in an ideal solution, G is at a minimum at X_i = 0.5 and a stable solid solution is predicted (e.g. forsterite – fayalite). G at the minima is strongly controlled by T.

Assuming simple binary mixing e.g. Fe-Mg in garnet



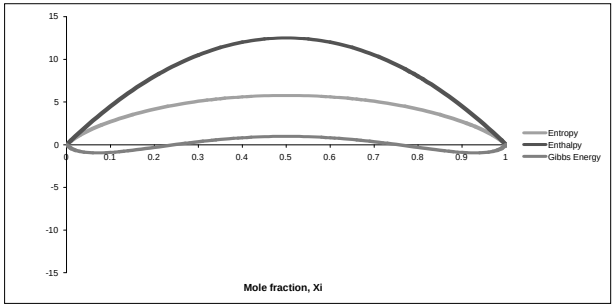
In the non-ideal case we add an excess energy term. A simple way of doing this is with a regular solution (e.g. Powell & Holland, 1993):

$$\overline{G}_{\text{Excess}} = \sum_{i=1}^{n-1} \sum_{j>1}^{n} X_i X_j W_{ij}$$

Where n = number of solution endmembers.

This effectively sums binary interaction energies across the entire phase

Assuming simple binary mixing e.g. Fe-Mg in garnet

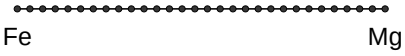


If the W_{ij} term (the Margules parameter) is strongly positive, the resultant G curve can develop two minima - a solvus is predicted.

Since the entropy term dominates at high T, solvii are predicted at low temperatures.

Solid solution models in Perple_X

- The pseudocompound approximation



- Auto refine and iteration

Extract from solution model file:

```
0. 1.   0.1 1
0. 1.   0.1 0
0. 1.   0.1 0
```

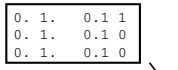
Auto_refine:

Run the entire calculation once at this resolution, find approximately where the ***actual*** compositional limits of each phase are, set these as the boundaries, increase the resolution over this smaller range, run again

Local Iteration:

Find out which pseudocompounds look most stable at each *PT* point, make more pseudocompounds close to these, throw away most of the others. Repeat this process several times for each *PT* point.

Extract from solution model file:



Auto_refine: In the "perplex_parameters.dat":

'auto_refine_factor_I' (and *II* & *III*) controls how much resolution is increased by after the first run (notice that *x/y_levels* and *grid_levels* have two sets of properties [pre- and post-refinement]).

Local Iteration : "perplex_parameters.dat":

'Iteration' has 3 values which control the number of times the compositions of stable phases will be refined, the increase in resolution between iterations and the number of 'unstable' pseudocompounds also refined.

These streamlining and iteration options are controlled from the 'perplex_parameter' file. They (hopefully) don't need changing too regularly…

Further reading:

Derivation of configurational entropy terms:

- Jamie Connolly's course notes (lecture 6)
- Spear, 1993, Metamorphic phase equilibria and *P-T-t* paths, first few pages of chapter 7.

Regular solution models:

- Powell & Holland, 1993, American Mineralogist, v78, 1174-1180.

Van Laar solution models:

- Holland & Powell, 2003, Contributions to Mineralogy & Petrology, v145, 492-501.