

Crust to Core workshop: An introduction to Perple_X

Seville, March 2009
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Crust to Core workshop: An introduction to Perple_X

Part 1: A very brief introduction

American Oxford Dictionary

Thermodynamics: the branch of physical science that deals with the relations between heat and other forms of energy (such as mechanical, electrical, or chemical energy), and, by extension, of the relationships and interconvertibility of all forms of energy.

An introduction to (or some revision on) thermodynamics

American Oxford Dictionary

The **first law of thermodynamics** states the equivalence of heat and work and reaffirms the principle of conservation of energy. The **second law** states that heat does not of itself pass from a cooler to a hotter body. Another, equivalent, formulation of the second law is that the entropy of a closed system can only increase. The **third law** (also called Nernst's heat theorem) states that it is impossible to reduce the temperature of a system to absolute zero in a finite number of operations.

An introduction to (or some revision on) thermodynamics: Some definitions

- A **system** is some part of the universe that you want to study and understand
- The **surroundings** are everything else in the universe that is not in our system
- The **system** can be *open* or *closed* to (*isolated from*) the surroundings in terms of both matter and energy

All Changes in a system are associated with the **transfer of energy**

Natural systems tend toward states of minimum energy

**An introduction to (or some revision on) thermodynamics:
Some definitions**

- In our case, a **system** is likely to be a mineral or a rock
- In this case, it is comprised of chemical **components** that describe chemical variability in that mineral or a rock
- Typical **components** might be FeO, MgO and SiO₂ used to describe olivine
- A **phase** is any mechanically separable and chemically homogenous portion of the system, e.g. a melt, a fluid, or a mineral in a rock
- A **reaction** is anything that changes the nature of the phases within a system

**An introduction to (or some revision on) thermodynamics:
Some definitions**

- Thermodynamics is primarily concerned with macroscopic energies of microscopic processes that we might or might not fully understand.
- It is convenient to group all of the variables required into two classes:

Intensive variables are independent of the amount of material present:

e.g. Pressure (*P*) & Temperature (*T*)

Extensive variables are dependent on the amount of material present:

e.g. Volume (*V*) & Entropy (*S*)

An introduction to (or some revision on) thermodynamics

First Law of thermodynamics:

The increase in the internal energy (***U***) of a thermodynamic system is equal to the amount of heat energy (***Q***) added to the system plus the work (***W***) done on the system by the surroundings.

$$0 = dQ + dW - dU$$

$$W(\text{J}) = N \cdot m = P \cdot V \quad (P = \text{force/area [N/m}^2\text{] and } V = \text{m}^3)$$

$$dU = dQ + PdV$$

An introduction to (or some revision on) thermodynamics

Second Law of thermodynamics:

This introduces the notion of entropy (***S***) which relates change in temperature (***T***) with the heat energy (***Q***) added to the system:

$$dS \geq \frac{dQ}{T}$$

Which can be substituted into the first law:

$$dU \leq TdS - PdV$$

An introduction to (or some revision on) thermodynamics

$dU \leq TdS - PdV$ tells us about the energetics of a system without chemical change (i.e. a homogenous phase with no compositional change during the process).

To describe energetic changes coming from mass transfer we use the concept of chemical potential (Gibbs, 1876)

$$\mu_i \equiv \left(\frac{\partial U}{\partial n_i} \right)_{S, V, \text{ other components}}$$

Summing the energies associated with all components in the system and adding to our combined laws equation yields

$$dU = TdS - PdV + \sum_{i=1}^k \mu_i dn_i$$

An introduction to (or some revision on) thermodynamics

$$dU = TdS - PdV + \sum_{i=1}^k \mu_i dn_i$$

Is the fundamental equation that we will use to quantify internal energy. This can be transformed to give various combinations of S , V , T and P as the independent variables.

$$\text{Gibbs free energy: } dG = -SdT + VdP + \sum_{i=1}^k \mu_i dn_i$$

Gibbs free energy will be of most interest to us, since P and T are the most obvious choices of independent variables for geologic application

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$$\text{Gibbs free energy: } dG = -SdT + VdP + \sum_{i=1}^k \mu_i dn_i$$

$$\left(\frac{\partial G}{\partial T} \right)_{P, n_i} = -S$$

Change in G with respect to *temperature* = *entropy*

$$\left(\frac{\partial G}{\partial P} \right)_{T, n_i} = V$$

Change in G with respect to *pressure* = *volume*

$$\frac{dP}{dT} = \frac{S_2 - S_1}{V_2 - V_1} \text{ (Clausius-Clapeyron)}$$

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$$\text{Gibbs free energy: } dG = -SdT + VdP + \sum_{i=1}^k \mu_i dn_i$$

Ignoring (for a while) heat capacity, thermal expansion and isothermal compression...

- If a chemically closed system has two possible states (configurations of phases), the one with the lowest absolute G at any PT should be more stable.
- If both have the same absolute G (the ΔG of moving from one state to the other = 0), they have the same relative stability and a reaction between them is stable.

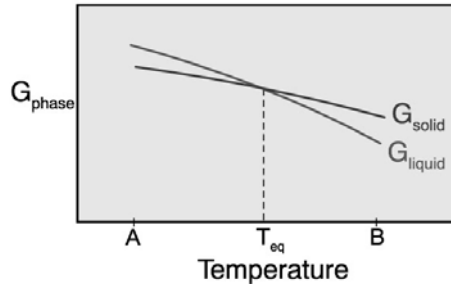
An introduction to (or some revision on) thermodynamics

$$\left(\frac{\partial G}{\partial T}\right)_{P, n_i} = -S, \text{ so } S_{\text{liquid}} > S_{\text{solid}}$$

A: Solid more stable than liquid (low T)
 B: Liquid more stable than solid (high T)

Equilibrium at T_{eq}
 $G_{\text{Liq}} = G_{\text{sol}}$

Melting reaction occurs at T_{eq}



Relationship between Gibbs free energy and temperature for the solid and liquid forms of a substance at constant pressure. After Winter (2001) An Introduction to Igneous and Metamorphic Petrology, Prentice Hall.

An introduction to (or some revision on) thermodynamics

Two fundamentally different approaches are commonly-used:

1. Find the lowest absolute G to predict the most stable configuration of phases:
 e.g. Perple_X (Connolly)
2. Find the reactions between phases by finding where G is equal between configurations ($\Delta G = 0$):
 e.g. THERMOCALC (Holland & Powell)

Both approaches are very simple for chemically simple systems, for example...

An introduction to (or some revision on) thermodynamics



$$-TS_{\text{Sillimanite}} + PV_{\text{Sillimanite}} = -TS_{\text{Andalusite}} + PV_{\text{Andalusite}}$$

If we know the entropy and volume of sillimanite and andalusite (which are PT dependent), we can easily calculate the PT line along which they both occur...



Useful resources:

- Frank Spear's book (*Metamorphic Phase Equilibria and Pressure-Temperature-Time Paths*) is good for the thermodynamic laws and their derivation (especially chapter 6).
- So are chapters 1-4 of Jamie Connolly's ETH course notes (http://www.perplex.ethz.ch/thermo_course)

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Part 2: The structure of a Perple_X calculation



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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., Petrin, 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.

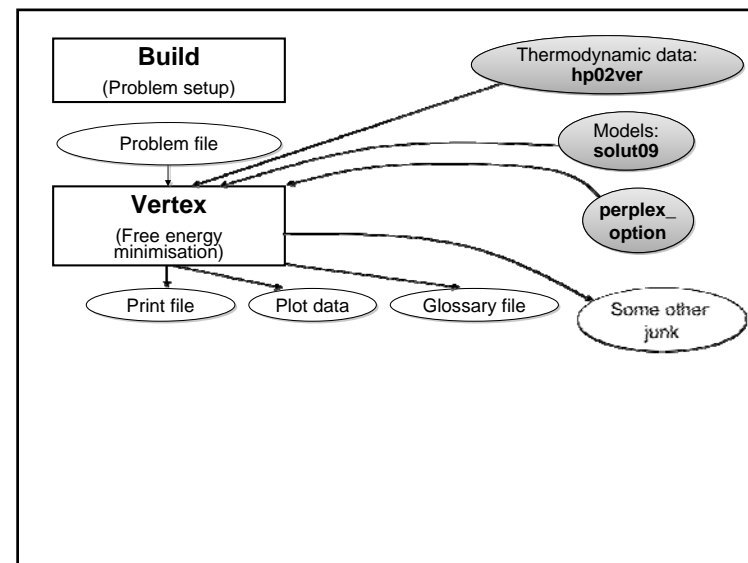
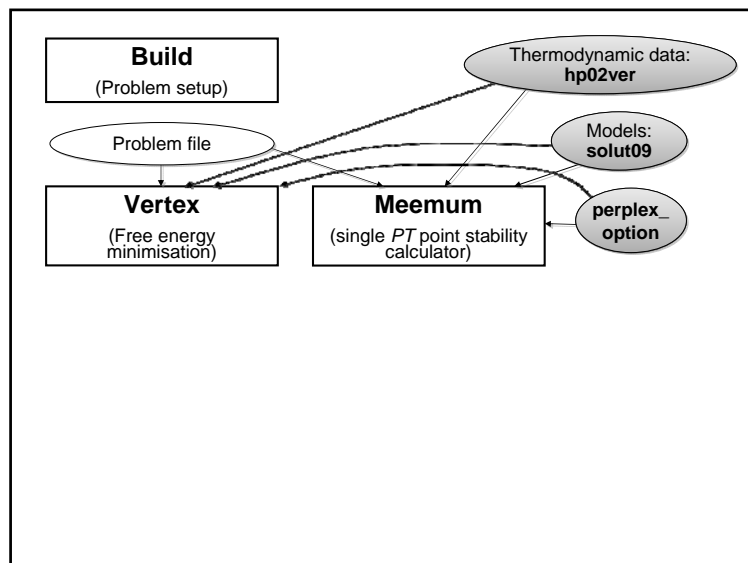
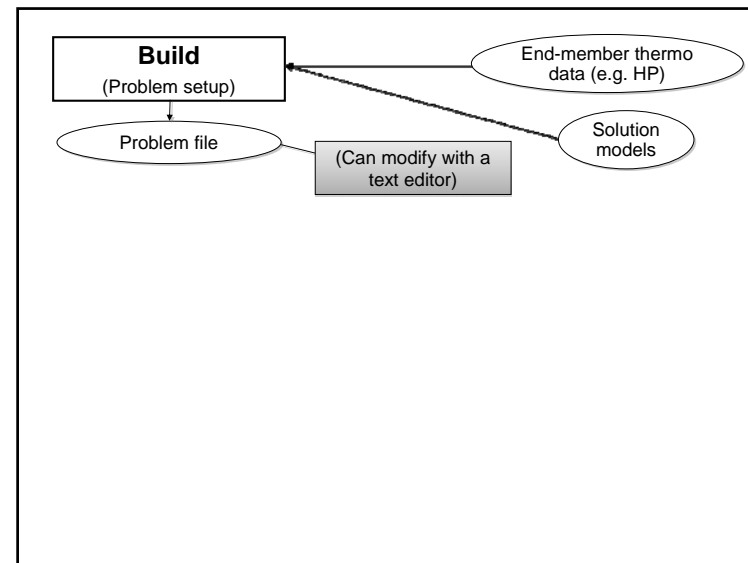
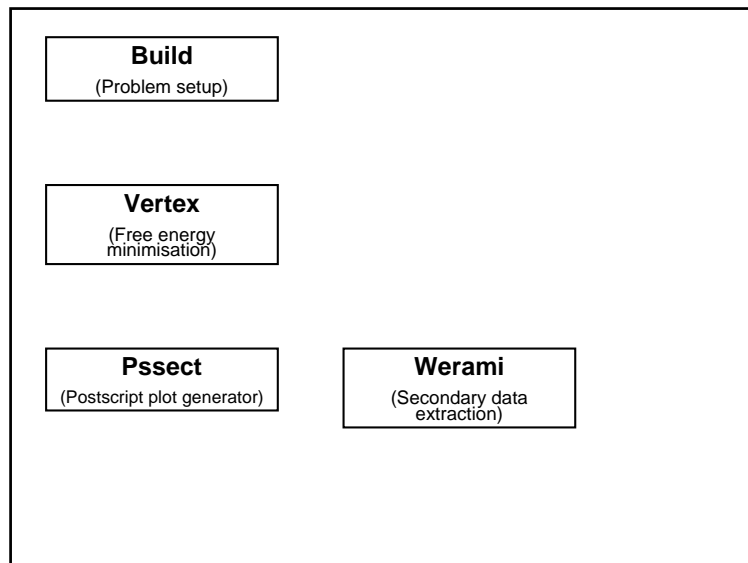
Caddick, M.J., Thompson, A.B., 2008. Quantifying the tectono-metamorphic evolution of pelitic rocks from a wide range of tectonic settings: Mineral compositions in equilibrium. *Contrib. Mineral. Petrol.* **156**, 177-195.

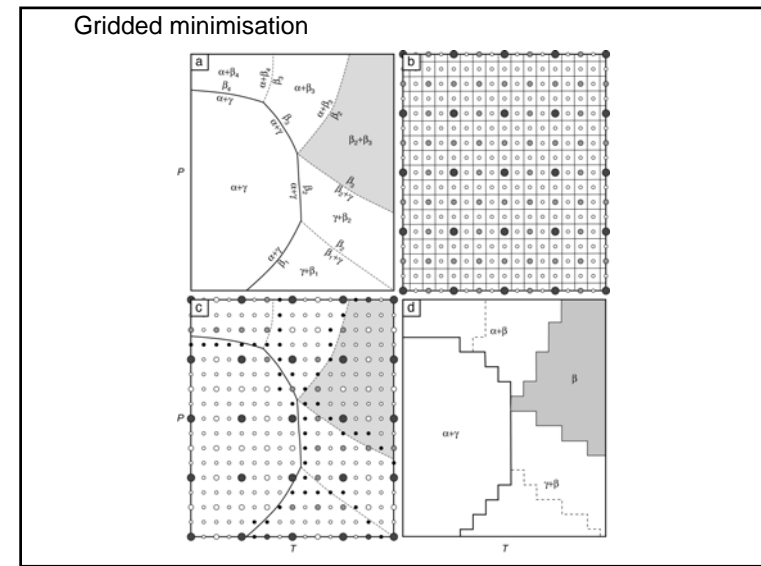
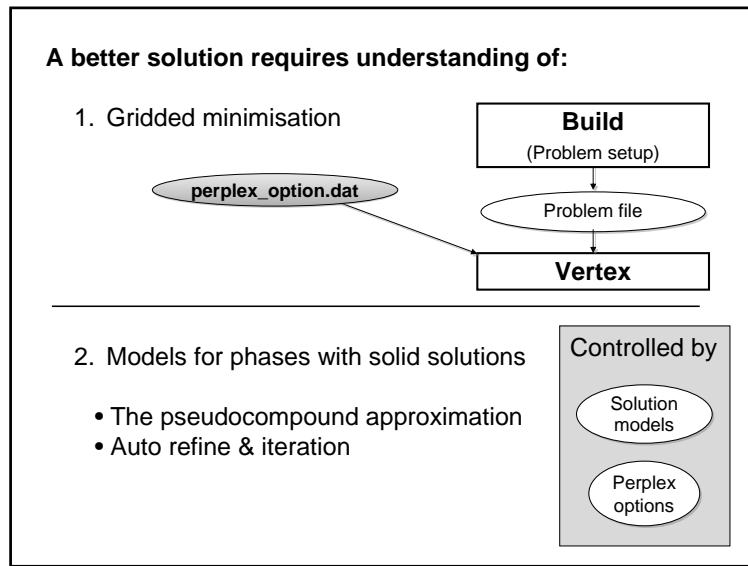
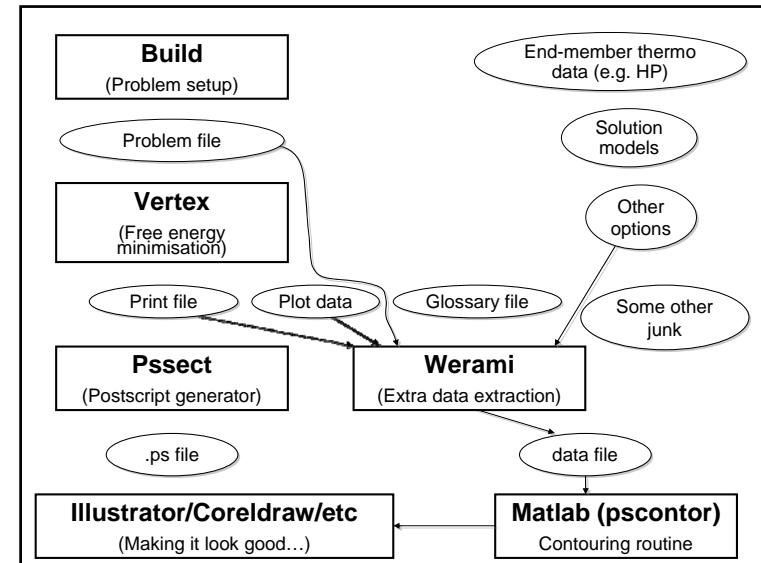
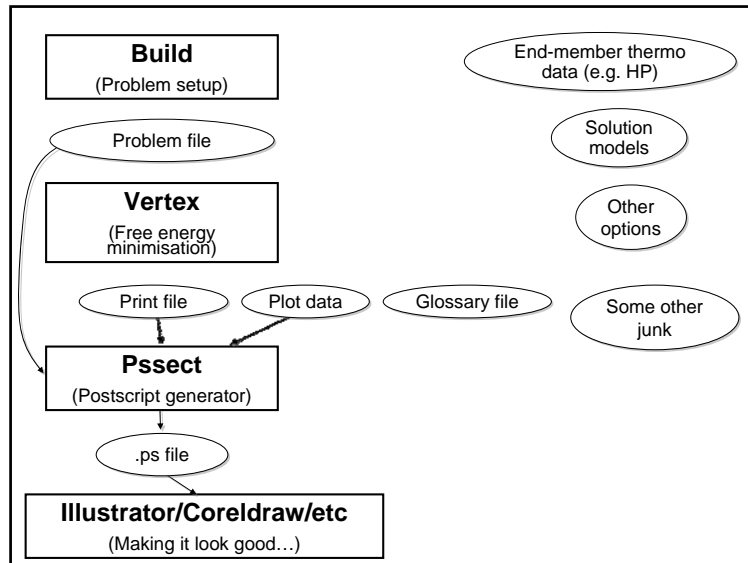
Perple_X:

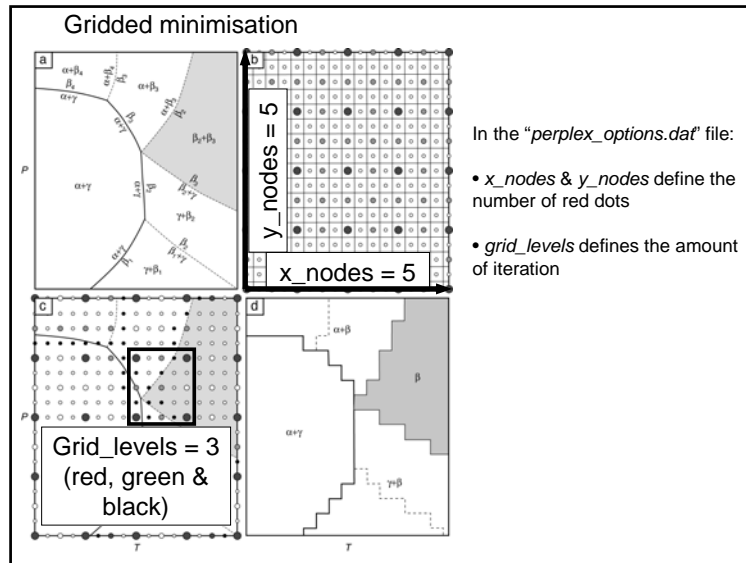
- Minimises free energy of multiple phase configurations to identify the 'most stable' set.
- Can work with complex phases by breaking solution-space into a number of discrete 'phases' (pseudo-compounds).
- Is very flexible, generating:
 - *PT* projections
 - Pseudosections
 - Compatibility diagrams (e.g. AFM triangles)
 - Mixed-variable diagrams
- Is very flexible, allowing:
 - Complex saturation hierarchies
 - Transformation of components
 - Use of numerous EOS for fluids involving H₂O, CO₂, 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.







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)

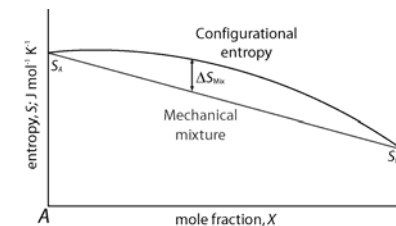
Three main types of solution model:

- **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 & Fe³⁺ -Al in garnet)
- **Multiple site** mixing requiring **charge balance** (e.g. NaSi -CaAl in plagioclase feldspar)

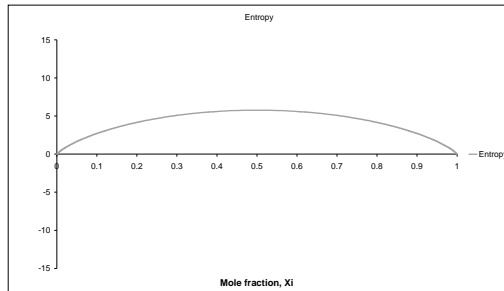
Assuming simple binary mixing e.g. Fe-Mg in garnet



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

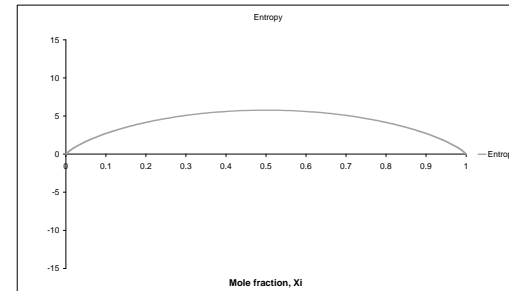


Configurational entropy is a function of disorder, so logically must be at a maximum when the $X_i = 0.5$. It follows that S_{config} must always be positive.

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

$$^2 \bar{S}_{\text{config}} = -\alpha_c R \sum_{i=1}^n X_i \ln X_i \quad \text{Where R is the gas constant and } \alpha_c \text{ is the site multiplicity}$$

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



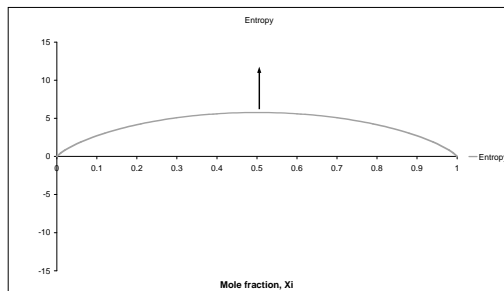
In our binary case:

$$^2 \bar{S}_{\text{Config}} = -\alpha_c R (X_A \ln X_A + X_B \ln X_B)$$

$$^2 \bar{S}_{\text{Config}} = -\alpha_c R (X_i \ln X_i + [1 - X_i] \ln [1 - X_i])$$

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

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

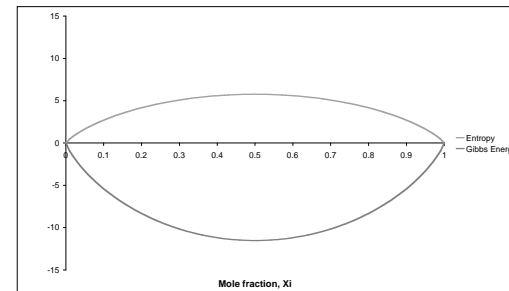


Entropy from multiple site mixing simply requires summing terms, e.g., for a phase with two distinct crystallographic sites:

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

$$^2 \bar{S}_{\text{Config}} = -R (\alpha X_A \ln X_A + \alpha X_B \ln X_B + \beta X_Y \ln X_Y + \beta X_Z \ln X_Z)$$

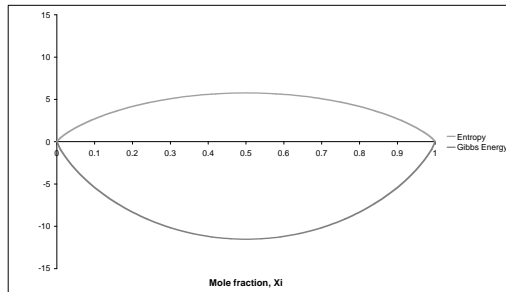
Assuming simple binary mixing e.g. Fe-Mg in garnet



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

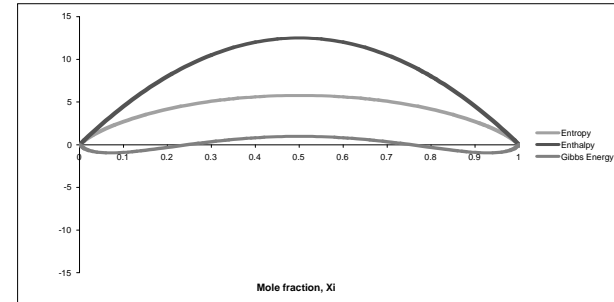


In the non-ideal case we add an excess energy term. A simple way of doing this is with a regular solution (e.g. Powell & Holland, 1993):

$${}^2 \bar{G}_{\text{Excess}} = \sum_{i=1}^{n-1} \sum_{j>1}^n X_i X_j W_{ij}$$

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

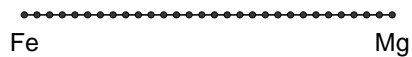


If the W_{ij} term (the Margules parameter) is strongly positive, the resultant G curve can develop two minima - a solvus is predicted.

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

Solid solution models in Perple_X

- The pseudocompound approximation



- Auto refine and iteration

Extract from solution model file:

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

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

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:

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

Auto_refine: In the "perplex_parameters.dat":

'*auto_refine_factor_1*' (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.

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Part 3: What data is Perple_X actually using?



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Perple_X finds an optimum set of pseudo-compounds for the P, T, X conditions of interest. This is based on available information on the H, S, V of end-members, combining these into solution-phases.

Ignoring some complexity (e.g. X), we could write a simple equilibria that we could solve by hand



$$-TS_{\text{Kyanite}} + PV_{\text{Kyanite}} = -TS_{\text{Sillimanite}} + PV_{\text{Sillimanite}}$$

It is univariant, so each P has one unique T at which this occurs, we just need S and V for each phase...

Extract of THERMOCALC molar thermodynamic properties, Table 5 of Holland & Powell, 1998

	H	$sd(H)$	S	V	a	b	c	d	$a\bar{u}$	κ	T_c	S_{max}	V_{max}
Kyanite	-2593.13	0.7	83.5	4.414	0.2794	-0.7124	-2055.6	-2.2894	4.04	1590			
Sillimanite	-2585.89	0.7	95.5	4.986	0.2802	-0.69	-1375.7	-2.3994	2.21	1320	2200	4	0.035

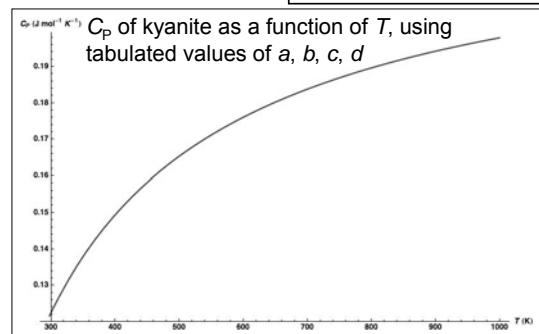
But these are the values for V, S (and H) at 25 °C, atmospheric pressure!

Extract of THERMOCALC molar thermodynamic properties, Table 5 of Holland & Powell, 1998

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$$C_p = a + bT + cT^{-2} + dT^{-1/2}$$

$$C_p = \text{J mol}^{-1} \text{K}^{-1}$$



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$$C_p = \text{J mol}^{-1} \text{K}^{-1}$$

$$S_T = S_0 + (S_{\text{Max}} / 1000)Q_{298}^2 + \int_{298}^T \frac{C_p}{T} dT$$

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$$S_T = S_0 + (S_{\text{Max}} / 1000)Q_{298}^2 + \int_{298}^T \frac{a + bT + cT^{-2} + dT^{-1/2}}{T} dT$$

$$S_T = S_0 + (S_{\text{Max}} / 1000)Q_{298}^2 + \left[a \ln\left(\frac{T}{298}\right) \right] + [b(T - 298)] - \frac{c}{2} \left(\frac{1}{T^2} - \frac{1}{298^2} \right) - 2d \left(\frac{1}{\sqrt{T}} - \frac{1}{\sqrt{298}} \right)$$

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$$V_{1,T} = V_0 + V_{\text{Max}} Q_{298}^2 \left[1 + a^\circ(T - 298) - 20a^\circ(\sqrt{T} - \sqrt{298}) \right]$$

V at 25 °C, 1 atm

Thermal expansivity, K⁻¹

V at T of interest, 1 atm

Extract of THERMOCALC molar thermodynamic properties, Table 5 of Holland & Powell, 1998

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$$V_{1,T} = (V_0 + V_{\text{Max}} Q_{298}^2) \left[1 + a^\circ(T - 298) - 20a^\circ(\sqrt{T} - \sqrt{298}) \right]$$

Bulk modulus (degree of incompressibility)

V at T of interest, 1 atm

Volume at the P and T of interest (based on the Murnaghan EoS)

$$\int_1^P v dP = \frac{V_{1,T} \kappa_T}{3} \left[\left(1 + \frac{4P}{\kappa_T} \right)^{3/4} - 1 \right]$$

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	H	$sd(H)$	S	V	a	b	c	d	$a\bar{u}$	κ	T_c	S_{max}	V_{max}
Kyanite	-2593.13	0.7	83.5	4.414	0.2794	-0.7124	-2055.6	-2.2894	4.04	1590			
Sillimanite	-2585.89	0.7	95.5	4.986	0.2802	-0.69	-1375.7	-2.3994	2.21	1320	2200	4	0.035

We can thus use the tabulated data, with the correct set of equations, to extrapolate the thermodynamic properties (V , S & H) to the P and T of interest - this is *part of* what THERMOCALC does.

This handling of data is explained more fully in:

HOLLAND, T. J. B. & POWELL, R. (1998), *J. Metamorphic Geology*, **v16**, 309-343.