Calculating mineral equilibria back

In the application of equilibrium thermodynamics to the calculation of phase diagrams, there are two approaches that can be followed: one based on the minimisation of Gibbs energy, the other being a derivative equivalent based on the solution of sets of non-linear equations. The main non-linear equations involved are the "equilibrium relationships": the relationships for balanced chemical reactions between the end-members of phases that are in equilibrium with each other:

$$0 = \Delta G^o + \mathrm{R}T \ln K \qquad (1)$$

In this, ΔG^o is the Gibbs energy of the reaction between the pure end-members in the same structure as the phases in which they occur, K is the equilibrium constant, in terms of the activities of the end-members in their phases, T is temperature, and R is the gas constant.

THERMOCALC follows this non-linear equation approach. Part of the reason for this was that, at the point when this facility was added to THERMOCALC in the late '80's, THERMOCALC aready was using a multi-equilibrium-relationship approach to geothermometry/barometry (the so-called average PT approach). Also it seemed to be the easiest way to draw, for example, PT projections.

The problem of calculating mineral equilibria can be thought of in terms of the number equations (constraints) involved and the number of unknowns being calculated. Average PT and phase diagram calculations may be contrasted, with the thing they have in common that each involves an independent set of reactions between the end-members of the phases involved in the equilibrium:

average PT The independent set of reactions involves the end-members in the minerals of the mineral assemblage that are assumed to have been in equilibrium with each other, *and* that are also present in the thermodynamic dataset (and that one can write the a-x relationships for). See Powell & Holland (1988, 1994) for the logic relating to independent sets of reactions. If there are n reactions in the independent set, then there are n (independent) equilibrium relationships. Given that the mineral compositions are known (eg analysed by elctron microprobe), then the activities are also known, so there n equations in the number of unknowns that are deemed to characterise the conditions of metamorphism. For example, the metamorphic fluid is reasonably assumed to be specified (eg as pure H_2O), then there are two variables, P and T. Average PT is the weighted least squares process of calculating an optimal PT from the n equilibrium relationships. Given that such calculations are always over-determined, with more constraints than unknowns, a statistical procedure should be involved in calculating the best values of the unknowns. Average PT involves finding the PT that involves the minimum displacement of the PT lines representing the equilibrium relationships, accounting for the uncertainties on the activities and thermodynamic data (see Powell & Holland, 1988, 1994).

phase diagram calculations The independent set of reactions involves the end-members in the minerals of the equilibrium being calculated. In contrast to the average PT case, the system of equations formed by the equilibrium relationships is either exactly determined (ie all the unknowns can be calculated), or is under-determined, requiring that one or more variables need to be specified, depending on the variance of the system. For an n component model system with p phases, the well-known expression for the variance is

$n - p + 2$. Whereas for pseudosections the non-linear equations are augmented by composition ones, for P–T projections and compatibility diagrams just equilibrium relationships are involved. Consider first the latter, simpler case. If phase k involves e_k end-members, then it involves $e_k - 1$ composition variables. For the p phases in the equilibrium, there will be $\sum_{k=1}^{p} e_k \equiv s$ end-members of phases, and $\sum_{k=1}^{p}(e_k - 1) = s - p$ composition variables. The number of reactions between the end-members that make up an independent set is the number of end-members minus the number of components, $s - n$ (Powell & Holland, 1988). Given that there is a non-linear equation for each reaction in the independent set, these relationships indicate how many unknowns can be solved for, and therefore how many must be set, because the $s - n$ equations can only be solved for $s - n$ unknowns. The number of things that have to be set in order for an equilibrium to be calculated can be represented in terms of degrees of freedom, equal to the number of unknowns, $(s - p) + 2$, minus the number of equations, $s - n$, giving $n - p + 2$. So the number of degrees of freedom is just the variance. Setting unknowns may involve setting P and/or T, or setting compositional variables, as would be done, for example, in calculating composition isopleths on a P–T diagram. Therefore, by variance, v:

$v = 0$. For an invariant equilibrium, a point on a P–T diagram, all the unknowns can be solved for. With no composition variables set, the equilibrium involves $n + 2$ phases; the P–T of the point, and the compositions of all the phases in the equilibrium, can be solved for. For c composition variables set, the equilibrium involves $n + 2 - c$ phases. For example, a divariant assemblage involving n phases, with 2 composition variables set, corresponding to the intersection of two isopleths, is (effectively) invariant, and the P–T and remaining composition variables of the equilibrium can be solved for.

$v = 1$. For a univariant equilibrium, a line on a P–T diagram, if one of the unknowns is set (i.e. one of P, T and the composition variables), then the remaining unknowns can be solved for. With no composition variables set, the equilibrium involves $n + 1$ phases, and, given, say, P, the T and the compositions of all of the phases can be solved for. For c composition variables set, the equilibrium involves $n + 1 - c$ phases. For example, a divariant assemblage involving n phases with 1 composition variable set, is a line on a P–T diagram (an isopleth), the equilibrium is (effectively) univariant and, given, say, P, the T and the remaining compositions of the phases can be solved for.

$v = v$. For a v-variant equilibrium, if v of the unknowns are set (i.e. v of P, T and the composition variables), then the remaining unknowns can be solved for. If there are no composition variables set, then $v \leq 2$, or the equations cannot be solved. With no composition variables set, the equilibrium involves $n + 2 - v$ phases; for c composition variables set, the equilibrium involves $n + 2 - v - c$ phases.

The calculation of P–T and T–x/P–X pseudosections with the non-linear equation approach involves augmenting the non-linear equations formed by the set of equilibrium relationships with a set of equations derived from mass balance constraints. For the specified bulk composition that is being used for the pseudosection, these additional equations relate the mole proportion of each component in the bulk composition with the sum of the calculated mineral compositions multiplied by their modal proportions. In other words, the bulk composition must be able to be made up of an assemblage of the phases of

interest. Of course the phases in the assemblage must each have non-negative modal proportions.

For the n-component system considered above, there will be a mass balance equation for each component, giving n equations additional to the equilibrium relationships involved. There are also p additional variables, the modes of the phases. Then the total number of equations is $s - n + n$, i.e. s equations, in $s - p + p + 2$, i.e. $s + 2$ unknowns. So, if two things are specified, the number of equations equals the number of unknowns *regardless of the number of phases involved*. This means that the compositions of the minerals and their modes can be calculated for an equilibrium of any variance at given PT, once a bulk composition is specified (see also Spear, 1986). Alternatively if two modes are specified, the compositions of the minerals, the remaining modes and the PT can be calculated. Further, if the modes are specified to be zero, then the PT corresponds to a point where 4 boundary lines come together on a pseudosection (for the variance of the highest variance field at the field being greater than 1).