Activity-composition relationships

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In the application of equilibrium thermodynamics, the starting point is the "equilibrium relationship": the relationship for a balanced chemical reaction between the end-members of phases that are in equilibrium with each other:

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

in which 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, reflecting the way the end-members mix in their respective phases as given by their activities, a_k, T is temperature, and R is the gas constant.

The activity-composition (a-x) relationships of the phases of interest are what is required in calculating the equilibrium constant, K, in (1). Given that using THERMOCALC involves you (or a wizard) coding the algebraic form of the activity-composition (a-x) relationships of the phases of interest into the datafile that THERMOCALC uses, this side of things is hard to ignore. However you may be able to get away with not getting on top of this if you are happy to use datafiles coded by others.

The formulation of a-x relationships

The formulation of a-x relationships involves some subtle concerns, and is not simply a matter of deciding what model to use to express non-ideality. The tjbh/rp approach can be summarised as follows:

- a-x relationships in "real" phases are effectively impossible to model theoretically, probably being dominated by strain on the scale of adjacent sites. So the approach used has to be empirical to an important extent.
- Activities are conventionally divided into an ideal mixing part (the ideal mixing activity, or thermodynamic mole fraction), and a non-ideal mixing part (the activity coefficient). The first, strictly, relates to the problem of how many ways the constituents can be assembled in the structure; the second relates to the energetics of the resulting mix. These *cannot* be independent, but we have little choice but to consider them to be so.
- Ideal mixing activities will be formulated using ideal-mixing-on-sites (regardless of how non-ideal the mixing in the phase is).
- Activity coefficients will be formulated independently from the ideal-mixing activities. We do this with the symmetric formalism (SF), which is just a macroscopic pair-wise symmetric ("regular") model between the end-members in the phase. There is an interaction energy, W_{ij} between each pair of end-members i-j. There are no higher order interaction terms: a complex phase is completely specified by its binaries.
- Generally the constraints on the thermodynamics of minerals are constraints on activities, not on their component parts. This would not be a problem if, say, the

mixing-on-sites aspect was completely specified. However, in more complex phases, particularly those that involve coupled substitutions and in which short-range order is likely to be important, using mixing on the actual number of sites may give ideal mixing activities that are too small, forcing the W's to be larger to compensate. If this problem is serious, we vary the way we write the ideal mixing activities, by implication choosing an *effective* number of sites on which mixing takes place. Alternatively we may choose to "power" the site fraction terms to a fraction of the correct number of sites, as we do for the tetrahedral terms in amphibole (see Powell & Holland, 1999, referenced below). The calibration of the activity coefficients (ie the values of the W's) is *not* independent of the formulation of the ideal mixing activities.

- Once the ideal-mixing-on-sites activity is written, and the non-ideality formulated, there is still the matter of calibrating the model (ie estimating the values of the interaction energies. When calibrating, there is a range of possible values for W_{ij} that we would not normally wish to go outside, unless there is very little solution between the i and j end-members. If i-j involves mixing on n sites, W_{ij} outside the range $\pm 20n$ is already large. If W_{ij} is $20n$ in a simple phase implies a solvus between end-members i and j with its top at about 1000°C. Very large positive or negative W's in a calibration may be flagging that the ideal mixing activity is not being best formulated. ($W_{ij} = 0$ means that i-j is ideal, implying that the substitution(s) in going from i to j are energetically easy. Fe–Mg, a relatively easy substitution, gives a W of the order of $2n$ to $4n$). (All energies in kJ).

- We prefer to make $W_{ij} \neq f(P, T)$, partly for simplicity (in reducing the number of things we need to know), but also because if the dependence is anything but tiny it implies that the a-x model has something wrong with it.

Using the symmetric formalism, the formulation (coding) of non-ideality is done automatically by THERMOCALC. All the user does is list the values of the interaction energies, and THERMOCALC does the rest.

A brief outline of the symmetric formalism

References relating to the symmetric formalism are

Powell, R, and Holland, TJB, 1993. On the formulation of simple mixing models for complex phases *American Mineralogist* **78**, 1174–1180.

Holland, TJB, and Powell, R, 1996. Thermodynamics of order-disorder in minerals. 1: symmetric formalism applied to minerals of fixed composition. 2: symmetric formalism applied to solid solutions. *American Mineralogist* **81**, 1413–1437.

Powell, R, and Holland, TJB, 1999. Relating formulations of the thermodynamics of mineral solid solutions: activity modelling of pyroxenes, amphiboles and micas. *American Mineralogist* **84**, 1–14.

The abstract of the 1993 paper says:

> In activity-composition relationships for multi-site phases, it often occurs that end-members possess individual sites which contain more than one element. For example, in hornblende, $Ca_2Mg_3[MgAl][AlSi_3]Si_4O_{22}(OH)_2$, the M2 site contains one Mg and one Al, and the T1 site contains one Al and three Si. In such cases, normalization is required to ensure that the ideal mixing activity and the activity coefficient of each end-member are each unity for the pure end-member. Such normalization is well-known for the former, but not for the latter. A new formulation of normalization for activity coefficients is presented. In the context of symmetric (regular and reciprocal) interactions, the formulation is used to show that the thermodynamics can always be written in terms of $\frac{1}{2}n(n-1)$ interaction parameters, where n is the minimum number of components needed to represent the composition of the phase. These macroscopic interaction parameters are particular linear combinations of the constituent regular and reciprocal model microscopic interaction parameters. With this, a further generalization leads to a dramatic simplification in the writing of activity coefficients: for any end-member, a, of a complex phase, including all symmetric microscopic interactions:
>
> $$RT \ln \gamma_{\mathrm{a}} = -\sum_i \sum_{j>i} (p_i^0 - p_i)(p_j^0 - p_j) W_{ij}$$
>
> in which p_k is the proportion of end-member, k, in the phase, p_k^0 is the value of p_k in pure a, and W_{ij} is the macroscopic interaction parameter for the ij binary. The summations are over an independent set of end-members chosen to represent the composition of the phase.

Although not referred to as the symmetric formalism in this abstract, this activity coefficient expression is at the core of the approach, particularly in that it involves *macroscopic* interaction energies, as well as the proportions of the end-members in an independent set representing the phase. Although the macroscopic formulation is motivated by a microscopic approach (in terms of same-site and cross-site interactions), it need not be considered to be restricted to this.

With the two 1996 papers, there is the big extension to the handling of order-disorder in minerals. The two abstracts are

> Thermodynamics of order-disorder in minerals may be handled with an approach in which the mineral is treated as a solid solution between an independent set of end-members with which the range of possible states of ordering of the phase can be represented. Thus a mineral of fixed composition (a 1-component phase), requiring s independent order parameters to represent the state of order in the mineral, will involve an independent set of $s+1$ end-members. This approach is applied via the symmetric formalism, with the entropy part of the Gibbs energy taken to be the ideal configurational entropy of mixing using a mixing on sites formulation, and the enthalpy part is taken to be that of a regular solution between the $s+1$ end-members. The symmetric formalism is shown to be formally identical to the generalised Bragg-Williams or point approximation, and its treatment of convergent and non-convergent

cation ordering is compared with that of Landau theory. Its flexibility in describing a wide range of order-disorder behaviour is illustrated with applications to sillimanite, spinel, albite and potassium feldspar, the latter two involving order parameter coupling.

and

The thermodynamics of order-disorder in mineral solid solutions are handled with the symmetric formalism in which the mineral is treated as a solid solution between an independent set of end-members with which the range of composition and states of ordering of the phase can be represented. An n-component mineral, requiring s independent order parameters to represent the state of order in the mineral, will involve an independent set of $n + s$ end-members. The symmetric formalism involves ideal mixing-on-sites with regular solution activity coefficients. It is applied to omphacite, orthopyroxene, Fe-Mg clinoamphibole and alkali feldspar. The model for omphacites, with a single order parameter, successfully produces the topology of paired miscibility gaps with tricritical points at their apices with a critical curve connecting them. Fe-Mg orthoproxene is shown to behave effectively as an ideal solution at all geologically-relevant temperatures. Cummingtonite-grunerite solid solutions are slightly positively non-ideal, in either a 2-site or a 3-site model. Na-K alkali feldspars with order parameter coupling involving tetrahedral site occupancies can show the essential topological relationships in this system, with only one independent binary interaction energy. The power of the symmetric formalism comes from the simplicity of its representation of the thermodynamics of minerals and its flexibility with few adjustable parameters.

The fourth of the papers shows how the symmetric formalism thermodynamic description works for different choices of the independent set of end-members used to represent a phase. From the abstract:

In a thermodynamic description of a mineral solid solution, it is usual to select a minimal group of end-members which constitute an independent set, and yet in practical calculations it frequently occurs that a different independent set or subset is required. Given the simplification of the symmetric formalism, it is straightforward to derive the enthalpies of formation of dependent end-members as well as the interaction energies between the end-members in the new independent set, in terms of those in the original set. For example, a simplified ternary solid solution of Fe-free Ca-amphiboles might be described with independent end-members tremolite, tschermakite and pargasite, and yet some calculations may require the use of end-members such as edenite or hornblende. Not only are their end-member properties dependent on those of the first three, but the mixing properties of any of the binary joins involving edenite or hornblende are dependent on those in the original independent set. Examples drawn from pyroxenes, amphiboles and biotite micas show that such dependencies may prove invaluable in using experimental information or heuristics to help constrain the mixing properties of complex solid solutions.

Further examples of the application of the symmetric formalism approach are to be found in

Holland, TJB, Baker, J, and Powell, R, 1998. Mixing properties and activity–composition relationships of chlorites in the system $MgO–Al_2O_3–SiO_2–H_2O$. *European Journal of Mineralogy*, **10**, 395–406.

White, RW, Powell, R, Holland, TJB, & Worley, B, 2000. The effect of TiO_2 and Fe_2O_3 on metapelitic assemblages at greenschist and amphibolite facies conditions: mineral equilibria calculations in the system $K_2O–FeO–MgO–Al_2O_3–SiO_2–H_2O–TiO_2–Fe_2O_3$. *Journal of Metamorphic Geology*, **18**, 497–511.

Dale, J., Holland, T.J.B.and Powell, R. 2000. Hornblende-garnet-plagioclase thermobarometry: a natural assemblage calibration of the thermodynamics of hornblende. *Contributions to Mineralogy and Petrology* **140**, 353–362.

White, RW, Powell, R, & Holland, TJB, 2001. Calculation of partial melting equilibria in the system $CaO–Na_2O–K_2O–FeO-MgO-Al_2O_3–SiO_2–H_2O$ (CNKFMASH). *Journal of Metamorphic Geology* **19**, 139–153.

Holland, TJB, & Powell, R, 2001. Calculation of phase relations involving haplogranitic melts using an internally-consistent thermodynamic dataset *Journal of Petrology* **42**, 673–684.

The DQF approach is of use in general (in combination with the symmetric formalism), and as a THERMOCALC coding mechanism:

Powell, R, 1987 Darken's quadratic formalism and the thermodynamics of minerals. *American Mineralogist* **72**, 1-11.

Holland, TJB, and Powell, R, 1992 Plagioclase feldspars: activity-composition relations based upon Darken's Quadratic Formalism and Landau theory. *American Mineralogist*, **77**, 53-61.

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