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The uncertainty of the standard entropy and its effect on petrological calculations

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Internally consistent thermodynamic data bases are now routinely used in the Earth sciences for investigating various petrological, geochemical and geophysical problems. In this regard, the central question is to what level of precision the standard entropy So should be known for petrological calculations. We have addressed this issue and have chosen as study cases the dehydration reaction muscovite = K-feldspar + corundum + H_2O, the Mg-Fe exchange reaction between garnet and biotite, the GASP-barometer (grossular = 3 anorthite + 2 kyanite + quartz) and the continuous reaction muscovite /paragonite + quartz = K-feldspar/albite + sillimanite + H_2O, and we have used Monte Carlo simulation to calculate the effect of uncertainties in So on reaction positions in P-T space.

It turns out that the standard entropy should be precise in the 0.1 percent range in order that uncertainty envelopes of calculated reaction positions are not too broad and phase diagrams would become meaningless. Current calorimetric methods are able to deliver entropies with that quality (e.g. Dachs and Benisek, 2011). So in internally consistent thermodynamic data bases is sometimes not sufficiently precise. In the case of mineral end-members where So has not been measured, entropy estimation schemes are sometimes used (e.g. in THERMOCALC). However, deviations from calorimetric values can be several percent and even up to $\sim$10% in some cases. One example is spessartine. Recent relaxation calorimetric measurements on synthetic spessartine give $S^\circ = 335.3$ J/mole/K (Dachs et al., 2009), whereas previous estimates were considerably removed from this value ($S^\circ = 367$ J/mole/K, Holland and Powell, 1998). Entropy estimation techniques are not able to deliver reliable entropies and they are no substitute for calorimetric measurements.

A further issue is the extrapolation of heat capacities to high temperatures outside the range where calorimetric data are available. This is important when e.g. calculating mantle phase equilibria. Here, it turns out that considerable differences in Cp values up to $\sim$ 15% may exist between various published Cp polynomials even for “well studied” phases like fayalite (Benisek et al., 2012).

It can be concluded that the present databases do not represent “the final word” on thermodynamic standard state and mixing properties but rather a necessary first step in a long and ongoing effort to deliver such properties of sufficient quality. Standard entropies can now be routinely determined from low-T relaxation calorimetry on mg-sized samples (e.g. Dachs and Bertoldi, 2005). High-T calorimetric work is urgently needed for better constraining heat capacity polynomials at high temperature. Well characterized solid-solutions should be studied by relaxation and solution calorimetry, IR and/or synchrotron techniques, as well as phase equilibrium experiments to better quantify the excess thermodynamic properties, which are still barely known for most solid-solutions.