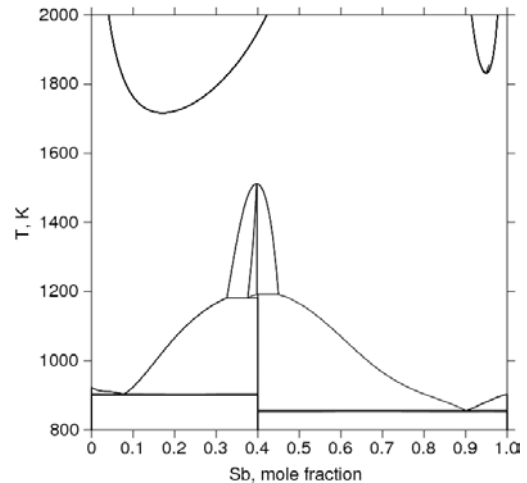


THERMODYNAMIC OPTIMIZATION UNDER TOPOLOGICAL CONSTRAINTS: PRINCIPLES AND EXAMPLES

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Sometimes a thermodynamic assessment leads to unexpected and unwanted artifacts. An inverted miscibility gap in the liquid phase at high temperatures is a frequent phantom of optimization. Figure shows the phase diagram of the Mg–Sb system calculated with interaction parameters from [1]. A good match between the calculated quantities and their experimental counterparts achieved in the optimization did not prevent an absurd feature Figure demonstrates. Other “unintended phase equilibria” mentioned in [2] are an unwanted existence of ordered phases and a reappearance of solid phases at high temperatures. There are cases when the liquid phase becomes stable again at low temperatures. Calculated phase boundaries with an excessive number of inflection points are also an undesirable assessment outcome. Optimization phantoms are not a mild irritant, but a grave concern since the Gibbs energies of phases resulted from the CALPHAD method are supposed to be usable beyond a range of conditions within which the experiments were performed.



Although an importance of this problem was understood while ago [3], the first method specially tailored to struggle against inverted miscibility gaps was proposed only two years ago [4]. Recently, a remarkably elegant Kaptay’s approach was tried for optimizing the Zn–Zr system [5].

A new method the presentation will be focused is different from the classical CALPHAD approach. The latter is essentially a non-linear least squares method, which minimizes a sum of weighted deviations of computed values from experimental ones. In addition to discrete experimental measurements and their accuracies, the method directly takes into account topological characteristics of thermodynamic properties and phase boundaries in the course of optimization.

It will be demonstrated that PARROT already has some of the features allowing one to carry out an optimization under topological constraints. Such an optimization performed for the Mg–Sb system resulted in an artifact-free description of the liquid phase.

In addition to the rigorous method of optimization under topological constraints, a simple heuristic trick of correcting the Gibbs energy of the liquid phase demonstrating a non-existing inverted miscibility gap will be outlined. The trick is especially useful when due to some reasons TCM and POP files used in the optimization are not available any longer.

References

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