Dear Stefan, Happy New Year! I should be celebrating but I wanted to get this done before our first anniversary (yes, I know, we sort of started in the beginning of Dec, however I don’t count that). I’ll send you a dropbox link to all the necessary files.

Some notes:

THE PROGRAM

1) the program is named MC\_fit and it and all the files it requires (and generated) are in stefan/MC\_inversion.

2) MC\_fit works by making NTRY starting guesses for the parameter values, each guess serves as a starting point from which it seeks to adjust the parameters so as to minimize an objective function that describes how well the prediction made from the parameters matches the experimental observations. This minimization is done by the Melder-Neade algorithm. The objective function accounts for observed vs predicted composition, if the prediction includes extraneous phases, and if the observation includes phases that are not predicted. This is essentially what Dean did in his 2022(1?) paper, except that in MC\_fit: it’s done entirely within Perplex rather than a mix of Matlab and Perplex, the objective function is modified slightly, the inversion is not Bayesian, and parameter errors can be estimated.

3) The primary input file with build (e.g., stinv\_mf.dat) specifies the chemical system, thermodynamic data source, solution models, etc.

4) An auxiliary file (e.g., stinv\_mf.imc) that specifies a) various algorithmic parameters; b) the parameters to be optimized; and c) the experimental data with uncertainties.

5) The output file (e.g., stinv\_mf.out) lists the best model found by each Nelder-Meade “Try”, the value of OBJ for the try is listed (be careful not to confuse this with the “Best OBJ so far value”). After the Try statistics, the scores for the individual experiments are listed, scores >1 indicate extraneous or missing phases. The scores for the prediction of extraneous phases are by their mass proportion, my idea being that a small amount of an extraneous phase should not be heavily penalized as it's possible the small amounts might not be observed. Thus if extraneous phases are present it's possible that the objective function can still have values <1. Scores for the failing to predict an observed phase are invariably > 1. If you want to see the details of the predicted assemblage to see why an observation has a high score use MEEMUM to reproduce the predicted assemblage.

6) It is possible to compute errors on the parameter estimates, however it’s slow and because of the strong covariance I’m not convinced they are particularly useful. I guess it’d be possible to actually compute the covariance matrix, though I haven’t set that up.

THE DATA

Your data has some issues, I’m inclined to believe that consequences are minor and need not be corrected. Specifically, in one-phase experiments you give a different bulk composition than you do for the single phase. This has the consequence that it is impossible to predict the phase composition from the bulk composition, thus even if the inversion predicts the phase perfectly, the observation gets a finite score (rather than zero as it should). A similar, correctable, issue exists for two phase experiments, in particular if the bulk composition and the composition of one phase are known, then the composition of the other phase is determined by mass balance. In principle the mass balance constraint (aka, the lever rule) can be applied to results with any number of phases but for more than 2 phases it’s not worth the trouble. For < 3 phases, who knows? probably not.

MY ANALYSIS

After some struggles I opted for a piecewise analysis, MF binary first, CF binary second, and ternary expts third. The reason for that approach was I couldn’t understand what was going on if I did everything all at once. The MF result is remarkably good, it’s particularly pleasing that a regular solution model for both the melt and Nin fits as well as more elaborate models. The CF result caused me endless headaches because I didn’t understand that the asymmetry of the eutectic could not be explained by 2nd order expansion, i.e., the asymmetry requires a 3rd order model for the liquid. I did not use a 3rd order model for the solid because the range of Nin (oldhamite) is limited in the CF experiments. Further it emerged that the excess terms needed to be temperature dependent to prevent extensive liquid immiscibility. This temperature dependence is poorly constrained by the limited T-range of your experiments, but the maximum likelihood CF model predicts only limited (acceptable in my view) immiscibility. I doubt the T dependence on CF Niningerite is necessary, I forgot to turn it off, if you repeat the analysis I’d leave it out. Given the limited amount of ternary data, and that the ternary interaction terms had little effect, I decided to eliminate the ternary interaction terms from my preferred model (stinv\_tern\_simpler), one outcome that I think has some credibility is an azeotrope in the CM liquid (which corresponds roughly to the trough in the ternary liquidus surface and, probably, the eutectic in CF. The extrapolations both to the CM join and the ternary liquidus are speculative, i.e., given the limited range of the data it can be fit almost equally well by a large range of models.

The files, program, and output for my inversion are in Stefan/MC\_inversion. More quantitative details are summarized in stinv\_tern\_SUMMARY\_OF\_CHOICES.bst.

Back calculated phase equilibria and the necessary files and programs are in Stefan/phase\_relations. The binary cases are relatively straight forward. Isobaric ternary diagrams can be calculated by either VERTEX or CONVEX. Those calculated with VERTEX tend do have minor glitches when the fields get very thin and, unfortunately, are drawn with on right triangles. Despite this they are my preference, you can import them into a graphics program (e.g., Coreldraw) and stretch them into equilateral triangles. Those calculated with CONVEX are messy, though equilateral and if you plot them with and without labels etc, they are clear. The advantage of convex is you can calculate a bunch of diagrams in one run. The liquidus surface is calculated with VERTEX, the output leaves something to be desired and while it gives you a rough idea of what’s going on, it’s probably easier to construct the liquidus from isobaric sections. The input file names (\*.dat) should tip you off as to which are which, I’ve also made \*.pdfs from the postscript output of PSSECT/PSVDRAW for further clarification. Jamie

P.S., This email is in Stefan/Stefan\_explanation.docx

P.P.S., If you decided to try an inversion yourself, then it might be interesting to do an all-in-one model rather than the piecewise strategy I used.

P.P.P.S., It’s just as well you did not go further with your maple script, I am pretty sure that you’d have had to change to a sub-regular model for the CF liquid. that’d not be a big deal, but every change creates the possibility for errors.