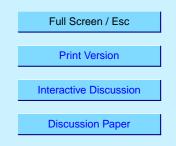**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "A computationally efficient inorganic atmospheric aerosol phase equilibrium model (UHAERO)" *by* N. R. Amundson et al.

Anonymous Referee #2

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General remarks:

This paper presents an inorganic equilibrium model which can accurately treat solution non-ideality, by using the Pitzer-Simonson-Clegg mole fraction based activity coefficient model, and at the same time is designed to be computationally efficient. Often there is a trade-off between these two model features that have in the past dictated the areas of applicability for the modelling framework. Indeed, it is the mathematical tools available to the community, or indeed known by the community, which I feel have hindered this marriage of accuracy and speed. For this reason I feel that this paper is

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particularly relevant. Indeed, aerosol science should extend into many focused disciplines, a perfect example given here. I have a few general points and specific remarks to address given below:

General comments and questions

1. The mathematical procedure stated in the paper has not been used in any other atmospheric equilibrium model. On that note it may be beneficial to elucidate on the advantage of this method over the other direct minimisation techniques. For example, what is the main feature that makes this technique more advantageous over the quadratic sequential programming methods used in AIM and ADDEM. The two papers you have referenced are extremely technical and are likely to be beyond the scope of the community as a whole so it simply may be beneficial to carry out this elucidation for the benefit of the ACPD readers. This leads onto my next question.

2. Is the mathematical technique easily extendible to any number of components. In other words, is it essentially a 'black box' algorithm which can be used with ease by the community, since use in larger scale modelling has been implied, should any activity coefficient model be required?

3. One of the benefits of this technique you have mentioned is the lack of any a-priori information regarding the phase state of the aerosol, unlike other models you listed in table1 designed specifically to improve performance. Have you tested whether an initial guess using the ZSR relationship can further improve performance? Or indeed, do you plan on testing this? Normally the ZSR can provide a good approximate first guess for both inorganic and organic systems.

4. One feature of the majority equilibrium models available, apart from ADDEM and the model of Ming and Russell (2001) (which hasn't been included in table 1) is the neglect of curvature. Have you thought about including this in your framework? If so, could either technique presented by the two models mentioned above be used in conjunction with your direct minimisation or is one framework preferable over the other?

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For example, from your Gibbs energy formulation, presumably you would encounter complex surface tension derivatives, thus in a sense, force you to use the iterative scheme employed in ADDEM.

4. You have referenced the use of extended UNIQUAC. Extended UNIQUAC combines UNIQUAC as the non-electrolyte part and an electrolyte part based on the Debye-Huckel theory. Firstly it may be better to use the earlier reference of Thomsen et al (1996) which describes the model in more detail.. Secondly, you have not stated why you have chosen it. Is it merely to illustrate that you can, or do you plan on including organics into the framework in the near future? If so then I would argue that this may be helpful for laboratory studies on 'simplified' systems but not ground breaking for atmospheric predictions given the lack of data from which important interaction parameters can be derived amongst other issues. Similarly there is the idea that interaction parameters derived from a subset of compositions do not necessarily work for the same species in more complex mixtures. Such is the basis of a vast composition matrix used for deriving interaction parameters for predictive UNIFAC. For your exUNIQUAC, predictions where did you get the interaction parameters from? If you do intend to utilise such an activity coefficient model, it should also be pointed out that UNIQUAC is not predictive, unlike UNIFAC (Fredenslund et al 1975) or LIFAC (Yan et al 1999), for example, which uses the UNIFAC model framework based on functionality. Since there is a severe lack experimental data for mixed inorganic-organic solutions, predictive models are likely to be preferential for future parameter fitting. Having said that however, an additive approach, not necessarily the same as a ZSR scheme, seems the only current option for a large portion of the aerosol composition space. There are a variety of mixed inorganic/organic activity coefficient models which have been available for some time and are currently being analysed for a range of simplified systems (see Raatikainen and Laaksonen (2005)). Has there been any comparisons between exUNIQUAC and the Pitzer-Simonson-Clegg model for multi-component inorganic mixtures since exUNIQUAC does not consider ternary interactions?

5. One general question connected to some of the above statements regards your thoughts regarding the inclusion of organics, and it should also be aimed at other models in the community. I understand that the complexities of including organics have been covered to some extent in some preceding equilibrium modelling papers, but I am curious as to whether this framework could easily accommodate this important fraction. For example, would you simply combine two separate minimisation routines, or modules, when calculating the associated water content?

Specific remarks.

Section 1-Table 1. You should include EQSAM (Metzger 2000) and the model of Ming and Russell (2001). Including EQSAM is particularly relevant since this was designed to provide an analytical solution to the gas-aerosol equilibrium problem thus improve efficiency considerably. However, it does include a variety of assumptions not employed in your model. It may be useful to highlight these differences and comment on how your model improves on that front. Indeed, do you know if EQSAM is going to be even more efficient than your scheme but clearly not as accurate for the given composition space?

Section 1 paragraph 3. There have been interesting studies showing that ambient and laboratory multi-component aerosols remain aqueous at low RH even in low temperature conditions (Pitchford and McMurry 1994, Dicket al 2000, Weingartner et al 2002, Marcolli et al 2004, Choi and Chan 2002) This is down to the complex interactions between the inorganic and oxidised organic fraction found in the atmosphere. I would assume that there is a dearth of data prohibiting one to use your model for mixed inorganic/organic crystallisation predictions. Indeed, it may not be necessary for a wide range of conditions, though I clearly understand that more ambient studies are required to quantify this effect. Do you feel that this predictive feature would be attainable for such mixed systems in the near future? What data is required to do this?

Section 2 - Determination of equilibrium. It should be stated that this minimisation formulation neglects curvature and is not a complete formulation. Thus it cannot be

extended to sub-100nm aerosol or indeed for activation predictions.

Section 2 paragraph 4. You state that ' The key parameters in the equilibrium calculation are the activity coefficients.' Whilst these parameters are indeed crucial, when it comes to treating solid precipitation, the two papers describing GFEMN and AD-DEM highlight a sensitivity in calculating the deliquescence points to tabulated values of the energies of formation for the inorganic salts. Indeed, a change in only 0.5% was enough to cause a significant increase/decrease in the calculated DRH point. You should state where you have taken the values from and report any similar sensitivity.

Section two paragraph 6. 'phase stability criteria are included..' What are these?

Section 3, paragraph 2 'Jo varies between 1024 and 1036, and we choose 1030 here'. Have you simply chosen the median value or does this hold any physical significance? On that note, have you conducted sensitivity studies to your crystallisation calculations by varying such parameters?

Section 3, paragraph4. It may be useful to elucidate further, i.e. provide the mathematical relationship, on how one can derive the surface tension of the crystalline germs from measured crystallisation points. As you have stated that this leads to an ability of calculating the surface tension of crystals, this may prove useful for models such as that of Ming and Russell(2001) or corroborate other studies (Ghosal and Hemminger1999; Weis and Ewing 1999; Russell and Ming 2002) where the influence of the surface energy of the crystal can be analysed or inferred from experimental data in relation to changing deliquescence points with changing aerosol dry size.

Section 4.paragraph 1. 'The system that is arguably the most important'. Ideally this should be changed to the inorganic system.

Section 4 paragraph3. Again as stated above, you should state where you got the appropriate energies of formation for the complex salts.

Section 5. When you state that each grid point requires an average of 4.25 Newton

iterations, and takes 4.3 seconds, for example, for analysing 104 points are you imply-ing that for each point the Pitzer-Simonson-Clegg mole fraction based model is called 4.25 times..thus leading to 4.25x104 evaluations in 4.3 seconds ?

Figures 1-11. Have u compared your predictions with AIM since the same activity co-efficient model is being used? Similarly, it may be useful to overlay one phase diagram using the Pitzer-Simonson-Clegg model and the exUNIQUAC model. It is important to analyse if the latter model can be used as it is presumably likely to be less computa-tionally expensive than the former.

There are quite a lot of figures on deliquescence but not a lot on efflorescence. Since it is a novel feature it might be better to show more examples.

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