**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "ISORROPIA II: a computationally efficient thermodynamic equilibrium model for K$^+$-Ca^{2+}–Mg^{2+}–NH$_4^+$–Na$^+$–SO$_4^{2-}$–NO$_3^-$–Cl$^-$–H$_2$O aerosols" *by* C. Fountoukis and A. Nenes

C. Fountoukis and A. Nenes

Received and published: 26 May 2007

Reply to reviewer #2

We thank the reviewer's thorough and thoughtful reviews.

General Comments This paper presents an improvement of the state-of-the-art thermodynamic module ISORROPIA for inorganic aerosols. The new version is Ě performed. The manuscript is well-written and its content is relevant for publication in ACP. Its importance in terms of modeling of inorganic aerosols is obvious. The references Ě benchmarked with SCAPE2. I will accept its publication after the completion of the

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following points by the authors.

The division of the aerosols into various modes, as a function of the ratios R1, R2, R3 or RH is artificial and probably source of non-negligible approximations. The authors do not discuss the sensitivity of the results with respect to the proposed thresholds. Since salts are expected to crystallize at equilibrium depending on the definition of the threshold, some examples, sitting at the limit between two different regimes should be provided to observe if discrepancies appear in the calculations (for instance between sulfate rich and sulfate poor aerosols) when considering two different set of equilibrium salts.

Reply: The reviewer poses a valid concern. There is the potential for some discontinuity for species that switch from being "minor" to "major" while transitioning over the threshold, (e.g., for NO3-(aq)). We have not observed such issues in water uptake or concentrations of crystallized salts (most likely because the water content is often enough at the transition point to completely dissolve salts).

ISORROPIA II assumes as an initial guess that all salts are crystallized. This initial guess is not very "physical". The authors pointed out that all the others models start from the opposite assumption. What is the advantage of taking this reverse approach in terms of modeling and computation?

Reply: We do not state that all other models adopt the opposite methodology. To address this, we explicitly state that SCAPE2 adopts the opposite methodology. Assuming the salts are initially crystallized may not seem "physical", but ensures that a minimum amount of water exists in the aerosol upon deliquescence. This enhances numerical stability, as the solution towards equilibrium just dissolves salts (or gas phase) species into a preexisting aqueous phase. The same cannot be said when assuming the aerosol is an aqueous phase.

Comparison with ISORROPIA. The extension in terms of incorporation of crustal species is clear. Although the authors compare the CPU performance of ISORROPIA

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II vs its previous version, there is no comparison of actual results for specific cases. These have to be added: does the second version give a more accurate solution or the same? are there differences in the iterations process? are the solutions consistent?

Reply: We do not show comparison of results from the two versions because they both give the same answer (when the concentration of crustal species is zero). In the absence of crustal species, there are no differences in the solution procedure.

Throughout the paper, the model uses precomputed data vs is real-time computations. A more precise summary of what is done in real time and what is precomputed would be interesting to estimate both computational costs.

Reply: The only precalculated data that can be used are lookup tables of binary activity coefficients, which decreases computation cost by roughly 30%. The user may of course choose to use online computations instead; this comment has been added to the manuscript.

Finally I share the opinion of a previous referee: for one given system, is the computational result accurate and how does it compare with actual data? This point has to be addressed.

Reply: That is indeed a good point. Although most of the papers describing aerosol models do not show comparison with known thermodynamic data we are including this comparison here (as suggested by the reviewer) for completeness. We show two sets of comparisons with known data. 1. We compare our model calculations with data from the literature for a variety of mixtures that include the new salts introduced in ISORROPIA-II. We compare mass fraction of solute predicted by ISORROPIA-II with measurements for a known T and composition of the liquid phase and for a wide range of water activities (RH). 2. We compare ISORROPIA-II predictions of aerosol water content in the mutual deliquescence region with measurements.

Specific Comments 1. In the introduction, the authors mention the global optimization

of a nonlinear convex problem. In fact, I think the function is not necessarily convex, but only locally convex. Could you comment?

Reply: It is indeed locally convex. We have modified the text to account for this.

2. In the same paragraph, the nonlinearity is assumed to be stronger for low RH and activity coefficients are used only in that case. When neglecting activity coefficients for high RH, are there inconsistencies in the results between low and high RH? The authors should precise how to define in a robust way the threshold between low and high RH (in others terms, when do activity coefficients have to be incorporated)?

Reply: We apologize for the confusion that this statement may have caused. Activity coefficients are always computed in ISORROPIA, regardless if RH is high or low. Therefore, inconsistencies do not arise.

3. In Section 2.4, the authors propose a ZSR approach for the calculation of the water uptake, the reason being that the direct computation of water activity is computationally expensive (although the reference they mention is pretty old). However, some of the methods appearing in the references have proved that this computation is tractable. Can the authors comment on the implementation of this additional computation? Did they try and if not do they plan to? What would be an estimation of the difference in CPU times?

Reply: Explicit water activity calculation is tractable, but still more expensive than ZSR, and this is why we choose the latter (and will continue to do so in the future). A comparison of the relative difference in CPU and thermodynamic solution is interesting, but have decided to leave it for a future manuscript.

4. On page 1906, the authors make some assumptions on the behavior of potassium for instance. Do these assumptions come from a lack of precision of the activity model or are they required for computational simplifications? In the latter case, what would be the additional computational effort if they are relaxed?

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Reply: These assumptions are done for computational speed (e.g. page 1906 for potassium), and are part of the method ISORROPIA uses. The alternative would be the use of a direct Gibbs free energy minimization algorithm which comes with a larger computational cost (e.g., Ansari A.S., and S.N. Pandis, An analysis of four models predicting the partitioning of semivolatile inorganic aerosol components, Aerosol Sci. Technol., 31, 129-153, 1999).

5. An option is used to "force" ISORROPIA II to conserve mass. Does it mean that, in general, that the method is not mass conservative? In that case, can you quantify and justify the loss of mass.

Reply: Conservation of mass is always used in ISORROPIA (and ISORROPIA II). However, sometimes round-off errors under conditions of very low RH may lead to slight mass imbalance (less than 0.001%). In these cases, the solution can be adjusted to ensure conservation of mass to machine (i.e., FORTRAN DOUBLE PRECISION) precision.

6. On page 1913, the authors mentioned the difference in ordering the associations with K. The two models are using a different ordering. Could you develop to justify why the ISORROPIA ordering is more appropriate. Is there a way to get rid of these assumptions on the ordering of species?

Reply: We suggest that "compositional invariance with RH cycling" would be a good method for determining the aerosol composition. This is because aerosol is exposed to many RH cycles throughout its lifetime, and the "invariant" solution will be a more realistic representation of composition in the atmosphere. For example, in an aerosol with e.g. 2 moles of K, 0.7 moles of SO_4, NO_3 and Cl, ISORROPIA-II predicts that K will preferentially associate with SO_4 to form K_2SO_4. The remaining of K will associate with NO_3 and Cl to form KNO_3 and KCl, as SO_4 (as H_2SO_4) is much less volatile than NO_3 (as HNO_3) and Cl (as HCl) when exposed to RH cycling. A way to get rid of these assumptions on the ordering of species is again the use of a direct Gibbs free

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energy minimization algorithm, which would increase the computational burden. We have re-written this paragraph adding this example to make it clearer.

Technical Corrections page 1899 : Van't Hoff equation ?

Reply: We are referring to eq. (3) in the manuscript.

2. page 1899 - lines 4 and 6 : spaces are missing.

Reply: Done.

3. page 1902 - line 22 : sentence is not clear to me.

Reply: In this sentence we state that the model uses a simplified approach (described by Eq. 18-22) to calculate water and species concentration in the mutual deliquescence region. We have rephrased this sentence to make it clear.

4. page 1904 ; last line : sentence is not clear to me.

Reply: We mean that based on the values of R1, R2, and R3, we have defined 5 composition domains into which certain species (and reactions) exist. These domains along with the possible species in each one of them are shown in Table 3. We have rephrased this sentence to make it clear.

5. page 1908 - line 14 : pKa ?

Reply: pKa = -log(Ka) , where Ka is the equilibrium constant of the reaction:

$CO_2(g) + H_2O <-> HCO_3- + H+$, given by the equation:

$Ka = [HCO_3-][H+]\gamma HCO_3- \gamma H+ / pCO_2 aw$. Added in the manuscript.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 1893, 2007.

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