**Atmospheric
Chemistry
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Discussions**

Interactive
Comment

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_2O aerosols" *by* C. Fountoukis and A. Nenes

C. Fountoukis and A. Nenes

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Reply to reviewer #1

We thank the reviewer's thorough and thoughtful reviews.

General Comment (1) Considering Ě importance. For instance, Trebs et al. (2005) and Metzger et al. (2006) have shown that the consideration of mineral cations K+ - Ca2+ - Mg2+ with SCAPE2 causes a larger discrepancy to the observed ammonium concentrations compared to ISORROPIA, if these compounds were neglected. The reason was Ěconsistently included. However, the new problem with ISORROPIA II is that the

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user has to be aware that the results may sometimes agree less well with observations even though the model has improved with respect to ISORROPIA. I therefore recommend to make this point Ě the ISORROPIA II developers to further include at least major organic acids.

Reply: Good point. We have cited Trebs et al. (2005) and Metzger et al. (2006) and added a comment on organic acids and K+ from biomass burning. More often than not however, including crustals will improve predictions. For example, Ansari and Pandis (1999), using SCAPE2, found a 14% improvement in predicted PM2.5 nitrate when considering crustals. Jacobson (1999), using EQUISOLV II, found that predicted nitrate and ammonium in Los Angeles were seriously affected by the presence of Ca2+ and Mg2+. Fountoukis et al. (2007) applied ISORROPIA-II for Mexico City aerosol during MILAGRO 2006 (which is known to have a large biomass burning component) and found that including crustal species significantly reduces the prediction error for ammonium and nitrate.

(2) The manuscript is mostly a technical description, as no new scientific results are presented. Therefore, I suggest to either present this work accordingly, i.e. by changing the title and introduction to include "Technical Note", or to add new scientific results, which would however require another iteration step in the review process.

Reply: The manuscript is far from being a technical note for many reasons, some of which are: a) A new thermodynamic model is presented (which according to published literature, merits publication as a manuscript). b) ISORROPIA and SCAPE, which have been widely used for years to simulate atmospheric partitioning of aerosol species, are carefully intercompared. Sources of prediction differences have been identified and described. c) Most of the papers describing aerosol thermodynamic models do not show comparison with known (laboratory) thermodynamic data. We are including such a comparison here for completeness.

(3) Furthermore, like most of the literature in this field, the manuscript is uncritical in ap-

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plying laboratory measurements of activity coefficients - central in aerosol equilibrium thermodynamics - to atmospheric conditions.

Reply: Excellent point. We have addressed these concerns as follows: a) 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). b) We compare ISORROPIA-II predictions of aerosol water content in the mutual deliquescence region with measurements.

The implicit assumption is that the activity coefficients, measured at a fixed water mass, are valid for conditions in which the water mass is variable, being a strong function of RH in the atmosphere (see Metzger and Lelieveld, 2007). Considering the two main assumptions on which ISORROPIA (and ISORROPIA II) builds, i.e. (1) equilibrium and (2) that the water activity (aw) equals the fractional relative humidity (aw=RH; Eq. 15) - both assumptions already imply Eq. (16) - it is assumed that the equilibrium relative humidity (ERH) determines the saturation molality. This is well known and has been shown to be a sufficient approximation for many atmospheric conditions by various research groups. However, it is usually overlooked that these assumptions also determine both solvent and solute activities, thus including activity coefficients. Therefore, in the atmosphere aerosol activity coefficients are a function of ERH. I recommend adding a remark in the manuscript that this is a model limitation that should be addressed in future (also with respect to the computational performance).

Reply: ISORROPIA, ISORROPIA-II (and all other comprehensive models) are built on a very sound thermodynamic framework which has been shown to work extremely well. This is far from being a limitation. Expressing activity coefficients as a function of ERH is at best, a reformulation of the theory.

Specific Comments Abstract: please delete last sentence (the computational perfor-

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mance is not really satisfactory for large scale air quality and atmospheric transport model)

Reply: The success of ISORROPIA, being used in many 3D air quality models (like CMAQ and PMCAMx) and GCMs (like GISS-CACTUS), is largely because it effectively balances rigor with computational speed. ISORROPIA-II carries the same attributes; our statement is therefore appropriate.

p1896, line 24-25: change sentence to: "EQSAM2 considers activity coefficients for (semi-) volatile compounds according to Metzger et al. (2002a) to solve the $NH_4^+/Na^+/NO_3^-/SO_4^{2-}/Cl^-/Ca^{2+}/Mg^{2+}/K^+/RCOO^-$ system; earlier versions were based on a simplified parameterization of the non-ideal solution properties that employed a relationship between activity coefficients and relative humidity (Metzger et al., 1999) and excluded mineral cations and organic acids".

Reply: We apologize for this oversight. Changes are incorporated as suggested.

p1896, p1896, line 25+: please add: "In comparison, EQSAM3 applies the thermodynamic principles as described in Metzger and Lelieveld (2007).

Reply: Done.

Section 2: please clarify throughout all subsections that you follow the "classical" approach.

Reply: We have been very clear already; no change made.

Section 2.3: please mention alternative concepts (mentioned above) and clarify the restriction/problems with the "classical" methods.

Reply: Using a well established and proven framework is not a problem. No changes made.

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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.

Jacobson, M.Z.: Studying the effect of calcium and magnesium on size-distributed nitrate and ammonium with EQUISOLV II, Atmos. Environ., 33, 3635-3649, 1999.

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Moya, M., Ansari, A.S., and Pandis, S.N.: Partitioning of nitrate and ammonium between the gas and particulate phases during the 1997 IMADA-AVER study in Mexico City, Atmos. Environ., 35, 1791-1804, 2001.

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