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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 #4

We thank the reviewer's thorough and thoughtful reviews.

Summary The introduction is clear and sufficiently comprehensive. I understand the need to compare efficiency and outputs to some benchmark model (which is done in section 4). However, this ms - and it is far from alone among papers describing atmospheric aerosol models - does not show a single comparison from which it is possible to tell how well the model (with its many assumptions) represents the known thermo-

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dynamic properties of at least some of the new mixtures that are represented. In this it differs markedly from most geochemical models (for brines and other natural waters), for which authors usually go to great pains to demonstrate how well/badly the models agree with the data. While the features and assumptions that go into ISORROPIA II seem to be quite clearly described, the reader cannot tell from this ms how well the model performs in this simple sense: for a known T and composition of a liquid phase how accurately does the model calculate the assemblage of salts and the water activity (RH) of the aqueous phase (if any)? Data with which to compare the model are certainly sparse, but they are not entirely absent. I can't recommend publication unless the authors address this issue.

Reply: The reviewer raises a very important point. As suggested, we are now including comparison 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). This comparison along with a discussion is shown below and has been added in the revised version of the manuscript.

Salts of calcium, magnesium and sodium with chlorides, nitrates and sulfates are very hygroscopic (Chan et al. 2000). It is useful to assess the capability of ISORROPIA-II to predict water activities of various aqueous mixtures of these salts. Water activities (aw) for such mixtures have been measured from dilute concentrations to high supersaturations using an electrodynamic balance (EDB), (Ha and Chan, 1999; Chan et al., 2000; Choi and Chan, 2002). This process involves evaporating a levitated droplet through a step decrease of the RH of the feed to the EDB. In this way the mass fraction of solute ($mfs = \text{mass of solute} / \text{mass of solute and water}$) as a function of RH (or aw) is obtained. Figure 3 shows comparison of mass fraction of solute as predicted by ISORROPIA-II and obtained by experimental data for a variety of mixtures considering equal molar composition. The experimental data used here have been taken from Ha and Chan (1999), Chan et al. (2000) and Choi and Chan (2002). RH ranged

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between 0.20 and 0.80 while measurements were made at room temperature (21 to 23°C). As seen in Fig. 3 ISORROPIA-II predictions agree well with water activity measurements with an average standard deviation (of the difference between predictions and measurements) of ± 0.018 . A noticeable deviation from the 1:1 line was found for the mixtures NaCl:MgSO₄ and NaCl:MgCl₂ for some of the data point (corresponding to low RH). This is due to partial crystallization at low RH as reported by Chan et al. (2000) for these mixtures. The rest of the mixtures were found not to crystallize even at RH = 30 or 20% (Ha and Chan, 1999; Chan et al., 2000; Choi and Chan, 2002).

Figure 3(added in the ms): Comparison of mass fraction of solute (mfs = mass of solute / mass of solute and water) as predicted by ISORROPIA-II (reverse mode, metastable state) and obtained from experimental measurements (Ha and Chan, 1999; Chan et al., 2000; Choi and Chan, 2002) for a variety of mixtures. RH ranged between 0.2 and 0.8 at room temperature. Equal molar composition is taken.

There are a number of other changes that need to be made:

The authors need to use subscripts (aq) (for aqueous ion) and (s) or (cr) (for crystalline solid) throughout the ms. There are too many cases where it is not clear whether they mean ion, species, electrolyte, or solid.

Reply: Done. We use (aq) for aqueous ions, and (s) for crystalline solids.

p1897: "forward" and "reverse" problems: some other models do both, and indeed are more flexible.

Reply: Of course.

after eq. 14: say "electrolyte" or "pair of ions" - as ion pair has another meaning.

Reply: Done

beginning of section 2.6: I would say "simultaneously saturated with respect to all components". The end of the sentence as written doesn't make sense. I do not have the

Nenes et al. (1998) paper to hand as I write, but I would like to see a practical example of eq (18), showing how well it works and comparing either with measurements (preferable) or, if not, with some model known to represent accurately the deliquescence properties of mixtures.

Reply: Good point. To address this concern, we add in the manuscript a section where we evaluate eq. (18), where predictions of ISORROPIA-II are compared with measurements for aerosol water content in the mutual deliquescence region. This is included in the revised manuscript.

Table 6 shows mass fraction of water ($\text{mfw} = \text{mass of water} / \text{mass of water and solute}$) for the $\text{NaNO}_3:\text{Ca}(\text{NO}_3)_2$ equal molar mixture. RH ranges between 0.246 and 0.461, which is below the DRH of $\text{Ca}(\text{NO}_3)_2$ (0.49) and considered to be in the mutual deliquescence region by ISORROPIA-II, hence eq (18) is used. The model is run in reverse mode and stable state (since the experimental data shown here correspond to a growth mode as described by Choi and Chan, 2002). As seen in Table 6, ISORROPIA-II agrees well with measurements of aerosol water in the mutual deliquescence region which shows that eq (18) approximates well the aerosol water content in this region.

Table 6(added in the ms): Mass fraction of water as predicted by ISORROPIA-II in the mutual deliquescence region and measured for an equal molar mixture of $\text{NaNO}_3:\text{Ca}(\text{NO}_3)_2$.

section 3: I believe a public comment has been made to the effect that hydrates are omitted from the list of solids included. This, as the authors must be aware, is a serious omission. There are many Ca^{2+} , Mg^{2+} and Na^+ salt hydrates that can form in the mixtures the model treats.

Reply: Comment is noted and addressed in the text. As stated in our response, potential formation of hydrated form of some salts has been neglected for computational efficiency purposes. The older version of ISORROPIA has been widely tested with observations and shown to perform very well (without considering the hydrated form of

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Na⁺ salts). While the presence of these species may theoretically change the partitioning of species, it is likely that for many atmospherically relevant conditions the effect of these species on model predictions is small (San Martini, 2004).

section 3.2: "The exact opposite methodology is adopted by other models". Not, I think, by all. Be specific.

Reply: We did not say by all; nevertheless we explicitly state "The exact opposite methodology is adopted by SCAPE2".

"compositional invariance with RH cycling". I'm not sure I understand this, but it doesn't seem like a "principle" to me. I assume "Na and K preferentially associate with SO₄..." just means that Na₂SO₄(s) and K₂SO₄(s) are less soluble than the nitrate and chloride salts. True enough. The description is sloppy: first the cations "preferentially associate" with sulphate, then they are "bound with NO₃ and Cl", then potassium "neutralises" sulphate, then it "reacts" with HNO₃ and HCl to form the solids KNO₃ and KCl. In the latter case I think the reaction would be with the anions. So what's going on? In addition to re-writing this paragraph the authors need to provide a couple of practical examples - with numbers - to show readers what this rule of thumb means. Finally - "sulphate is less volatile than NO₃...". The authors mean that SO₄, as H₂SO₄, is involatile in the model (unlike HNO₃).

Reply: We suggest that "compositional invariance with RH cycling" would be a good (i.e., computationally efficient) 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 SO₄, NO₃ and Cl, ISORROPIA-II predicts that K will preferentially associate with SO₄ to form K₂SO₄. The remaining of K will associate with NO₃ and Cl to form KNO₃ and KCl, as SO₄ (as H₂SO₄) is much less volatile than NO₃ (as HNO₃) and Cl (as HCl) when exposed to RH cycling. A way to get rid of these assumptions on the ordering of species is again

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

p 1907. CaSO_4 is assumed to be completely insoluble. So what happens in an aerosol with, say, a small SO_4^{2-} amount and a larger amount of Ca^{2+} ? Is *all* the sulphate assumed to exist as $\text{CaSO}_4(\text{s})$ at all RH? Or is this tied up with the description of the solution as a combination of various electrolytes (which can be done in different ways) rather than simply amounts of ions, and CaSO_4 is not considered? Explain.

Reply: In a case like that all the sulfate is assumed to exist as $\text{CaSO}_4(\text{s})$ and the remaining of Ca associates with nitrates and chlorides, either in solution or in the solid phase.

"Crustals" - there is no such noun. The authors variously mean crustal species, elements, cations or anions. Be specific throughout.

Reply: Done.

Section 4. This section is quite detailed, and clearly a lot of effort has gone into it. But I can't tell which is the more accurate model - there are some results described where ISORROPIA seems to give the more plausible result, but there are no data to show it.

Reply: The evaluation of ISORROPIA-II's accuracy requires a very extensive intercomparison with "comprehensive" models and observational data. This is clearly a task that cannot be a subject of one paper alone. The purpose of this section is not to identify the "most accurate" model but to compare predictions between the two models and understand the discrepancies (section 4.2). Clearly, SCAPE2 seems to have some problems at low RH (and ISORROPIA-II gives more reasonable results) but overall the two models agree well.

The way the model calculates the formation of solids is obscured, not clarified, by the description at the bottom of p 1913 where first of all Na is described as "partitioning"

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between NaNO_3 and NaCl - presumably the solids - then immediately afterwards the authors refer to the "dissociation" of NaCl(s) . Clarify.

Reply: Good point. Bottom of page 1913 corrected to: "the association of sodium between nitrate ($\text{NaNO}_3(\text{s})$) and chloride (NaCl(s))". The way the model calculates the formation of solids is very clearly described through Table 3, the 3 characteristic ratios and the compositional invariance with RH cycling.

References

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