

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

Anonymous Referee #4

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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 thermodynamic 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.

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.

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

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

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.

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 Ca²⁺, Mg²⁺ and Na⁺ salt hydrates that can form in the mixtures the model treats.

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

"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).

p 1907. CaSO₄ is assumed to be completely insoluble. So what happens in an aerosol with, say, a small SO₄²⁻ amount and a larger amount of Ca²⁺? Is **all** the sulphate assumed to exist as CaSO₄(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 CaSO₄ is not considered? Explain.

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

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. 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" between NaNO₃ and NaCl - presumably the solids - then immediately afterwards the authors refer to the "dissociation" of NaCl(s). Clarify.

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