

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 #3

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General Comments:

This paper presents an enhanced version of the equilibrium inorganic aerosol model ISORROPIA that explicitly includes the crustal cations K^+ , Ca^{2+} and Mg^{2+} . The model is compared to SCAPE2 over a range of atmospherically relevant conditions. The paper describes an important advance in the modeling of atmospheric aerosols. I recommend the paper be published with minor revisions, addressed below.

Specific Comments:

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The goal of this paper is to demonstrate the incorporation of atmospherically relevant crustal species (K^+ , Ca^{2+} , Mg^{2+}) into ISORROPIA. This is important for the reasons discussed in the paper. While the paper clearly describes why incorporating these species into a model is important, it would be useful if the authors quantitatively demonstrate the effect of explicitly including crustal species. I recommend that the authors consider comparing the modeling predictions of ISOPRIA-II not only against SCAPE2 but also against the 'old' version of ISORROPIA, where the crustal species are treated as equivalent sodium. This will answer the question of how much difference it makes to treat the crustal species explicitly versus as equivalent sodium.

I suggest that the authors acknowledge that double salt and hydrate species have not been incorporated into ISORROPIA-II. However, neglecting these species is not a major model weakness. Double salt and hydrate species have been observed in the laboratory (e.g., Potucki and Wexler, 1995; Koloustou-Vakakis and Rood, 1994; Klaue and Dannecker, 1993, 1994; Xu et al., 1998; Imre et al., 1997) and the field (e.g., Harrison and Sturges, 1984; Tani et al., 1983). While the presence of these species may theoretically change the partitioning of species and the aerosol water content, it is likely that for many atmospherically relevant conditions the effect of these species on model predictions will be small (San Martini, 2004; Wexler and Clegg, 2002).

I particularly applaud the authors' focus on computational speed, a key requirement to integrating an equilibrium aerosol code into an air shed model.

The authors have not mentioned an additional characteristic of ISORROPIA that makes its use particularly appealing: it is freely available via anonymous ftp. For a variety of reasons, other models are not as freely available. Making ISORROPIA so easily available is commendable.

1910/19-21: The authors may wish to consider not using the normalized mean error (NME) for their evaluation, as the use of NME may artificially weight overpredictions. Seigneur et al. (2000) recommend using average fractional bias and average fractional

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gross error.

It would be useful if the authors provided information on the ionic strength of the aqueous aerosol, especially for low RH regimes. This may help provide context for the discrepancies the authors found between the models at low RH regimes (1911/11-12). The discussion of stable vs. metastable solutions (Section 4.3) would also benefit from including information on the predicted ionic strength.

Technical Corrections:

1895/25-27: I suggest clarifying the sentence:

The non-linearity is stronger under conditions of low relative humidity, where aqueous aerosol solutions are strongly non-ideal and require the use of activity coefficients (which increases computational cost).

I think the key here is that at low relative humidities aqueous aerosol solutions are highly concentrated (i.e., have a high ionic strength). Under these conditions the solutions may behave non-ideally. This non-ideality is modeled with activity coefficients.

1896/14 omit the word 'have'

1897/12-17. Specify the outputs of the reverse problem.

1897/27-29: The authors may want to consider additional references that have examined using equivalent sodium. For example, this reviewer knows of another study that found that including crustal species as sodium equivalents reduces the bias and error for nitrate but does not improve overall model performance (and may sometimes affect the predicted response of inorganic aerosol to changes in precursor concentrations).

1899/13 As written, γ_i is actually the mean activity coefficient of species i . In order to be consistent with the notation in Section 2.3, I suggest you refer to electrolyte species as ij and hence activity is $a_{ij} = ((m_i \gamma_i)^{\nu_i})((m_j \gamma_j)^{\nu_j})$

1907/13: Is CaSO₄ assumed to be insoluble because it forms CaSO₄.2H₂O?

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1912/18-20: I do not understand your logic here. If SCAPE2 tries to solve for the aqueous case, hence deviating from the stable solution, should not the MNE be smaller when ISORROPIA II is run in the metastable branch?

1912-1914/Section 4.2: The entire section, while being relatively clear, would benefit from some editing.

1915/2: Should read whether.

Figure 3 and 4. Either add units to ordinate and abscissa of all plots or specify in the figure caption that all concentrations are $\mu\text{g}/\text{m}^3$.

Figure 3f. and 4f: What does a plot comparing the pH predicted by SCAPE2 and ISORROPIA-II look like?

Figure 8: The figure makes it appear that that the concentration of water and potassium goes briefly below zero just below 40% RH. This is just a function of the graphics program, but it would be nice to fix.

Final Random Question:

1896/16-17. Is the following statement correct? “Even though direct minimization usually gives the most accurate results, it comes at a large computational cost (Ansari and Pandis, 1999b).”

Thermodynamic equilibrium can be calculated either via the use of equilibrium constants or via direct Gibbs free energy minimization. Is one approach theoretically better than the other, or is it just that the computational implementation differs? For example, a series of approximations were made when formulating ISORROPIA-II to enhance its computational efficiency. If these approximations were not made, would the predictions between ISORROPIA-II and a model that directly minimized the Gibbs free energy be any different? Also, does Gibbs free energy minimization necessarily imply large computational costs? GFEMN was designed as a reference model and makes no effort to be computationally efficient (it walks through the entire solution space to find the

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minimum). AIM2 also uses a direct Gibbs free energy minimization. How does the computational efficiency of AIM2 compare with that of, for example, SCAPE2?

References:

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

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