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Atmospheric
Chemistry
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Discussions

Interactive comment on “Reformulating atmospheric aerosol thermodynamics and hygroscopic growth into haze and clouds” *by* S. Metzger and J. Lelieveld

S. Metzger and J. Lelieveld

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We thank Dr. Zaveri for his comments although the “several serious issues that must be addressed and clarified before EQSAM3 can be used with any confidence" are based on misunderstandings of our work and the available literature.

R. Zaveri: Point 1. "It is not clear how the calculation of aerosol water content in EQSAM3 is conceptually any different (and more efficient) than what is being done in most aerosol models available in the literature."

Reply.

- Our manuscript focuses on the calculation of aerosol water content, i.e. pages 853-

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870. How that is applied in EQSAM3 is described in on pages 870-876. None of this has been published previously.

- For the first time aerosol molality is explicitly calculated from the (measured) solute solubility and not based on polynomial fits to water activity measurements, which are available or used only for a limited number of compounds (compare e.g. Table 2 and 3). We explicitly account for the hygroscopicity of solute(s), which not only covers a wide range of inorganic salt compounds but also organic salt compounds. However, due to the lack of water activity data for many of the compounds listed in Table 1, we can so far only make predictions.

Any constructive contribution on this would therefore be highly appreciated.

- The concept of how aerosol molality and water activity are applied in EQSAM3 differs from other thermodynamic gas/aerosol partitioning models relying on the equilibrium assumption. For details we refer to Section 4 (pages 870-874) and Section 5 (pages 882-890) which summarizes key differences.

R. Zaveri: Point 1. "For example, on page 860, section 3, the authors talk about reformulating the classical treatment of equilibrium thermodynamics of atmospheric aerosols into something that consistently treats aerosol water. However, their supposedly new approach looks exactly like the widely used ZSR method in which single salt molalities mss(aw) at a given water activity aw (with aw = RH) are used to estimate the total water content. The ZSR equation looks identical to equation (23) derived in this paper (page 869, line 6). The authors eventually admit this on page 871, line 11, but then what is the new concept here.

Reply.

- Page 860 (section 3) states what makes our approach new, i.e. that "the water needed for hydration is directly proportional to the amount of solute, determined by the solute specific constants, independent of the solute concentration." How much water is needed for hydration of a specific salt compound was shown and derived in section 2, pages 853-860, whereby we explicitly account for the amount of water required to hydrate the solute in the equilibrium reactions. This is not only new, but also requires (allows) reformulation of chemical equilibrium.

- Regarding the ZSR-relation we state (page 871, point 4): "The water mass of single solute and mixed solutions is computed according to Eqs. (22) and (23)". Note that Eq. (23) directly follows from the principles of an osmotic system, i.e. from the additivity of the partial pressures, a consequence of the gas-solution analogy. Note further that Eq. (23) is equivalent to the ZSR-relation, an assumption on the additivity of partial water masses widely used in atmospheric modeling, as empirically established by Zdanovskii (1948); Stokes and Robinson (1966)."

- Thus, Eq. (23) depends on Eq. (22), which involves Eq. (20) and the prior equations, by which all Eqns except Eq. (23) are new. The fact that our new approach yields comparable results to other equilibrium models (section 4.2, pages 875-876) is remarkable, and demonstrates that even substantially different methods can give comparable results. The advantage of our method however is its computational efficiency.

- Any difference in the equilibrium molalities to other models or observations can easily be adjusted by using a correction factor (or new value) of the solubility value listed in table 1 (and used in EQSAM3). If, for instance 13.67 mol/kg (derived accord. to eq. (20)) would be inacceptable for one or the other application, it is very easy to use a different solubility value than the one listed in Table 1 (and taken from the CRC-Handbook of Chemistry to start with). However, the whole EQSAM3 concept will therefore not change, and should not be questioned.

R. Zaveri: Point 2. "A similar argument can be made for the treatment of activity coefficients."

Reply. Yes, but only if the concept is not understood. We will explain below why.

R. Zaveri: Point 2 (continued). "While expressing binary activity coefficients as a function of aw is indeed a rather clever approach, ..."

R. Zaveri: Point 2 (continued). "... the EQSAM3 model simply assumes that activity coefficients of electrolytes in a multicomponent mixture equal to binary activity coefficients values as a function of aw. This is not always a good assumption. Zaveri et al. (2005) clearly showed that multicomponent activity coefficients in representative salt mixtures can be significantly different than the binary values, especially at RH below 80%. "On page 889, line 4, the authors state that Zaveri et al. (2005) applied the activity coefficient methods to laboratory conditions without the required transformation to the atmosphere. This is simply incorrect. Zaveri et al. (2005) evaluated different activity coefficient methods under atmospheric conditions, with water activity aw = RH. Water content was also computed with the ZSR equation under atmospheric conditions, using single solute molalities evaluated as a function of aw (with a= RH). All this is very clearly stated in the paper."

Reply.

This statement indicates that our method is not understood.

It is not sufficient to only use the water activity as a function of RH (aw = RH) to account for the required transformation of laboratory conditions to the atmosphere. The reason is that the activity coefficient methods that have been applied in e.g. Zaveri et al. (2005) all (except the one of Metzger et al, 2002) rely on laboratory measurements from which either polynomial fits to various activity coefficient data have been derived to extent the concentration range of the solution.

In the atmosphere the situation is different, because the water uptake is a function of both the solute hygroscopicity and the water vapor concentration (not only RH due to the limit of the saturation vapor concentration). All aqueous aerosol properties therefore depend on the water content, whereby the aerosol molality is governed by RH. This clearly is different to the lab. While an increase in RH usually leads to additional water uptake, a decrease in RH causes either solute precipitation or evaporation in case of (semi-)volatile compounds and hence a decrease in aerosol water. By assuming equilibrium, however, it is implicitly required that the ion product is kept constant at a given RH (maintained either by solute precipitation or evaporation).

Under ambient atmospheric conditions, one should rather question the applicability of the equilibrium assumption. This should and will be discussed separately. However, as an approximation for aerosol-cloud coupling in climate and meso-scale models, the equilibrium assumption suffices for most applications. We explicitly compute the aerosol water uptake of individual salt compounds, and we make predictions for compounds for which we do not have water activity measurements (stated on page 867).

R. Zaveri: Point 3. "There are several problems in the way solid-liquid partitioning is treated in EQSAM3 .... ".

Reply.

The solid-liquid or liquid-solid partitioning is not entirely resolved for mixed compounds since it would require solubility measurements, partly unavailable. This may be discussed and we are open for suggestions and predictions of RHDs or MDRHs and their validation. However, the basic concept of EQSAM3 is not affected by potential uncertainties wrt MDRH predictions. Note that our concept, as applied in EQSAM3, allows to predict the RHD of individual inorganic salt compounds, which is also new, and may be further useful to predict the RHDs of individual organic salt compounds.

A constructive discussion on this issue would be highly appreciated.

R. Zaveri: Point 4. "It is not at all clear how EQSAM3 analytically and non-iteratively computes multicomponent gas-particle partitioning over size-distributed aerosol particles. Gas particle partitioning over size-distributed aerosols is a competitive, dynamic process in which aerosol particles of different sizes have different time scales to reach equilibrium with respect to the gas-phase species."

Reply.

-The EQSAM3 concept wrt solving analytically and non-iteratively multicomponent gas-particle partitioning is similar to that used by previous EQSAM versions, meanwhile widely applied in atmospheric models. For EQSAM3, this is summarized in section 4 (pages 870-876).

- Although gas-particle partitioning over size-distributed aerosol particles is not a principle limitation, it is not addressed in the present work; it obviously needs consideration of the size distribution. This application will be presented in a follow-up paper.

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