

Interactive comment on “A comparison of water uptake by aerosols using two thermodynamic models” by L. Xu et al.

Anonymous Referee #3

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I have read the Discussion paper, and posted Comments. I support of the Comment of Lescroart et al., and their analysis of the model of Metzger and co-workers. It is unusual that an "applied" ms be criticised in this way (that one of the models is flawed), but I think it is justified. I do not think the published Reply addresses the fundamental problems identified.

I returned to the 2007 ACP paper of Metzger and Lelieveld that described their model, which seemed little changed from the Discussion paper that had been quite strongly criticised by some reviewers.

Briefly, the application of osmosis to the gas/liquid equilibrium problem seems misconceived. The authors' work also make much use of the term "hydration", and refer to water being "consumed" and hydration "driving hygroscopic growth" without it having

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any recognisable meaning. (Activity coefficient models that take into account, or are based upon, the formation of hydration shells around solute ions do exist. EQSAM3 appears to have no relation to them.)

The authors claim the occurrence of their process of "hydration" renders standard thermodynamic treatments (which treat water primarily as a solvent medium) as somehow inconsistent and, by implication, wrong. This is not correct.

Examining some of the related material I see a number of what seem to be clear errors: the reaction (R1) is not an equilibrium expression as far as I can tell, and appears to combine a dissolution reaction with the dissociation of water. Equation (K1) appears to equate the product of two equilibrium constants with the *sums* of the species involved (rather than their product). Later, following eq (K2), the activity product of water (about 10^{*-14} at 25 oC) appears to be equated to water activity. Equation (15) appears to equate solvent and solute activities to each other in saturated solutions. Solute activity coefficients are described as being functions of solubility, which is more or less a reversal of the true relation. (Are solute and solvent activities related through the Gibbs-Duhem equation in this model?) An assumed partial dissociation of electrolytes is apparently involved in the EQSAM3 approach, too, but there appears to be no calculation or consideration of the equilibrium between undissociated and dissociated forms.

It is clear to me that either there is something fundamental about their method that the authors are not able to explain clearly, or there are basic flaws in their approach and they do not fully understand the principles of equilibrium thermodynamics. There are various general claims throughout the ms that make me fear the latter. These include, for example, statements that the Kelvin effect and Kohler equation are somehow redundant when using EQSAM3, and that other atmospheric modellers have not appreciated the significance of atmospheric RH (hence water activity) as a key variable, rather than solute concentration. Nor, apparently, have other scientists "consistently transformed the basic principles of thermodynamics to atmospheric modelling applications."

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Irrespective of the validity of comparisons between EQSAM3 and EQUISOLV, and the accuracy with which they have been carried out, EQSAM3 seems not to be - as Lescroart et al. state - a thermodynamic model. That is to say, it is not based upon thermodynamic principles and therefore cannot be relied upon.

The authors of the present Discussion paper have clearly put a lot of effort into their work. The only substantive criticism I'd make against it is that the differences between EQSAM3 and EQUISOLV should have been investigated further, by comparing with reference data. However, I regret that I have to recommend that the paper should not be accepted, for the reasons given above. It is my opinion that the reviewing process failed in the case of the 2007 paper by Metzger and Lelieveld describing EQSAM3. If it had worked properly then one of two things would be true: (1) there would be an EQSAM3 model that was both comprehensible and validated, and it would be possible to review the present ms on its own merits. Alternatively, (2) there would be no such model and this Discussion would not be taking place. I believe that to publish further studies involving EQSAM3 is almost certainly to perpetuate an error.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 9551, 2009.

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