**Atmospheric
Chemistry
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Discussions**

Interactive
Comment

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

L. Xu et al.

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L. Xu, J. E. Penner, S. Metzger, and J. Lelieveld:

Reply to the critical remarks by reviewer 3. Please also note our reply to Lescroart and colleagues, which complements the present reply.

Reviewer3: 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. . .

Reply: Here and in the complementing replies in the interactive discussion we argue that it is not justified to state that '. . . to publish further studies involving EQSAM3 is almost certainly to perpetuate an error'.

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Clearly, the "concept" brought forward in ML07 (http://www.atmos-chem-phys.net/7/3163/2007/acp-7-3163-2007.html) is not understood, either not well communicated or otherwise. We acknowledge that the different issues brought forward in ML07, i.e. osmosis and hydration, the new stoichiometric constant of water ν_w and the generalized mole fraction, the calculations of single solute molality and aerosol water mass, humidity of deliquescence (RHD) and efflorescence (RHcr), as well as the EQSAM3 model description represent aspects that require testing.

In the present context of the paper by Xu et al we test the application of eqs 19-23 of ML07 as used in EQSAM3, and it would be fair to review that aspect rather than all other issues brought forward and which are not relevant here. It is our hypothesis that EQSAM3 can reproduce many of the features described by detailed thermodynamics models; and that should be the subject of the discussion. We accept that EQSAM3, and in fact eq 19 of ML07, has not been derived on the basis of conventional thermo-dynamics, and will therefore refrain from calling EQSAM3 a "thermodynamics model". Since this seems to be the main issue throughout the interactive discussion, we hope this relieves the debate. Moreover, if given sufficient time by the editor, we plan to add an Appendix to the paper which explains the derivation of all equations applied in EQSAM3 (sec. 4.1 of ML07), in more detail than was provided in the original ML07 paper.

Our goal is to use EQSAM3 in global 3D applications for which many detailed thermo-dynamics models are unsuited as they are too CPU time demanding. We do not dis-pute that other models are more accurate (notably E-AIM); however, our "claim" is that EQSAM3 is sufficiently accurate to be used in 3D models for particular applications, which should be defined for the application in question. A main and limiting assump-tion is that of thermodynamical equilibrium. ML07 attempts to consistently apply this assumption to help formulate generalizations.

One can pursue this goal by simplifying detailed models, include look-up tables and define chemical domains for which additional simplifications can be made, whereas

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ML07 introduced a stoichiometric coefficient for water, ν_w. We realize that its derivation should be discussed in view of the important arguments brought forward by referee 3 and others. Any help from the chemical thermodynamics community would be highly appreciated. Thus, for the time being we accept that eq. 19 can be classified as an "empirical fit", a "semi-empirical expression" or a "parameterization" (we don't really care), as used in EQSAM3.

We nevertheless emphasize that the eqs 19-23 by ML07 predict the RHD, the aerosol associated water and other important parameters remarkably well, both for single solutes and mixed solutions, based only on the solubilities of the compounds involved. We are puzzled and disappointed by the interactive discussion that this aspect is ignored. We would welcome pursuing test cases defined by the reviewers (and others) to falsify that EQSAM3 can in fact predict the above parameters.

Further, we will work on the manuscript, in which a range of test cases have been defined, to help reveal strengths and weaknesses of the model (including possible programming errors and oversimplifications).

The customary procedure for reviewing the Xu et al. manuscript would be that the model is judged upon its predictive capability. It is important to disentangle the "concept" discussion from the model application in the present manuscript by Xu et al.

Thus we suggest decoupling the EQSAM3 application by Xu et al. from the thermodynamic principles questioned by referee3, who includes issues such as hydration, the Kelvin effect and the Köhler equation. These issues are not addressed in the manuscript by Xu et al. and are not relevant for the review.

Finally, we emphasize that EQSAM (versions 1-3) has already been successfully applied in 3D model applications as reported in the peer-reviewed literature (see below). This is the first paper to present a side-by-side comparison of the EQSAM3 model with a published model, which has been compared to other thermodynamic models including the "benchmark" AIM model (Zhang et al., 2000). The reviewer's final remark that

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"..to publish further studies involving EQSAM3 is almost certainly to perpetuate an error" seems inappropriate, since the model is already used in a variety of publications, whereas this is the first such study that includes a comparison of the EQSAM3 model with another model.

Several publications (not a complete reference list) which report the successful application EQSAM:

Jeuken, A., P. Veefkind, F. Dentener, S. Metzger, and C. Robles-Gonzales, Simulation of the aerosol optical depth over Europe for August 1997 and a comparison with observations, J Geophys. Res., 106, 28,295-28,311, 2001.

Metzger, S. M., F. J. Dentener, J. Lelieveld, and S. N. Pandis, Gas/aerosol partitioning I: a computationally efficient model, J Geophys. Res., 107, D16, 10.1029/2001JD001102, http://www.agu.org/journals/jd/jd0216/2001JD001102/index.html, 2002a.

Metzger, S. M., F. J. Dentener, A. Jeuken, and M. Krol, J. Lelieveld, Gas/aerosol partitioning II: global modeling results, J Geophys. Res., 107, D16, 10.1029/2001JD001103, http://www.agu.org/journals/jd/jd0216/2001JD001103/index.html, 2002b.

Lauer, A., J. Hendricks, I. Ackermann, B. Schell, H. Hass, S. Metzger, Simulating aerosol microphysics with the ECHAM/MADE GCM - Part I: Model description and comparison with observations, ACP, Vol.5, pp. 3251-3276, http://direct.sref.org/1680-7324/acp/2005-5-3251, 2005.

Trebs, I., S. Metzger, F. X. Meixner, G. Helas, A. Hoffer, M. O. Andreae, M. A.L. Moura, R. S. da Silva (Jr.), J. Slanina, Y. Rudich, A. Falkovich, P. Artaxo, The NH_4^+-NO_3^--Cl^--SO_4^{2--}-H_2O system and its gas phase precursors at a rural site in the Amazon Basin: How relevant are crustal species and soluble organic compounds?, J Geophys. Res.-Atmos., 110 (D07303), doi:10.1029/2004JD005478,

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http://www.agu.org/journals/jd/jd0507/2004JD005478/, 2005.

EMEP publications. The aerosol composition model EQSAM (Metzger et al., 2002a) is included in the Unified EMEP model, which is the most recent model of the EMEP Integrated Assessment Models. For results of a model comparison of the hemispheric version of the Unified EMEP model with various measurements including EMEP and GAW (Global Atmospheric Watch) databases, see EMEP publications, and in particular the EMEP MSC-W Technical Report, February 2006.

Metzger, S., N. Mihalopoulos, and J. Lelieveld, Importance of mineral cations and organics in gas-aerosol partitioning of reactive nitrogen compounds: case study based on MINOS results, Atmos. Chem. Phys., 6, 2549-2567, http://www.atmos-chemphys.net/6/2549/2006/acp-6-2549-2006.html, 2006.

Myhre, G., A. Grini, S. Metzger, Modelling of nitrate and ammonium-containing, aerosols in presence of sea salt, ACP, Vol.6, pp. 4809-4821, http://direct.sref.org/1680-7324/acp/2006-6-4809, 2006.

Tsigaridis, K., M. Krol, F. J. Dentener, Y. Balkanski, J. Lathiere, S. Metzger, D. A. Hauglustaine and M. Kanakidou, Change in global aerosol composition since preindustrial times, ACP Vol.6, pp. 5143-5162, http://direct.sref.org/1680-7324/acp/2006-6-5143, 2006.

Luo, C., C. S. Zender, H. Bian, and S. Metzger, Role of ammonia chemistry and coarse mode aerosols in global climatological inorganic aerosol distributions, Atmos. Environmen., 41(12), 2510-2533, 2007. PDF (Atm. Env.) ($^{©}$ 2006 Elsevier Ltd.)

Bauer, S. E., M. I. Mishchenko, A. A. Lacis, S. Zhang, J. Perlwitz, and S. M. Metzger , Do sulfate and nitrate coatings on mineral dust have important effects on radiative properties and climate modeling?, J Geophys. Res., http://www.agu.org/pubs/crossref/2007/2005JD006977.shtml, J. Geophys. Res., 112, D06307, doi:10.1029/2005JD006977, 2007.

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Bauer, S. E., D. Koch, N. Unger, S. M. Metzger, D. T. Shindell, and D. G. Streets, Nitrate aerosols today and in 2030: a global simulation including aerosols and tropospheric ozone, Atmos. Chem. Phys., http://www.atmos-chem-phys.net/7/5043/2007/acp-7-5043-2007.html, Vol.7, pp. 5043-5059, 2007.

Detailed Response to concerns of Reviewer 3:

Reviewer 3: 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 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.

Reply: In contrast to other approaches, EQSAM3 calculates the single solute concentrations from the compound's solubility and the newly introduced stoichiometric coefficient of water, ν_w. ν_w has been introduced by ML07 to represent on a stoichiometrical basis the degree to which water is 'consumed' in a chemical process that potentially involves solvation, hydration, hydrolysis, or any other process. These associated processes are traditionally neglected in a stoichiometrical notation of chemical reactions, and hence, activity coefficient models are needed. Instead, EQSAM3 does not require activity coefficients for non-volatile compounds, because ν_w is related only to the solute solubility.

As noted above, we hope to make the derivation on which the EQSAM3 model stands clear in the proposed Appendix.

Reviewer 3: Examining some of the related material I see a number of what seem

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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.

Reply: Equation R1 combines the change of the concentration of the solvent, i.e. the number of 'free' water molecules, when a solute is added that dissolves and dissociates either partly or completely because some of the 'free' water molecules are 'bound' to the solute either as a hydration shell, or because water is 'consumed' by associated hydrolysis, or by any other process (e.g. crystal water). Important here is only that both changes (number of moles of solvent and solute) occur simultaneously during the dissolution of a solute, and that both changes are related and can hence be expressed in terms of each other at equilibrium, if the stoichiometric coefficient of water, ν_w, is used.

Reviewer 3: 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.

Reply: Equation (K1) was in error in the original ML2007 manuscript. It should have been:

$$K_{NaCl_{(cr)}} \times \mathsf{K}_{H_2O_{(aq)}} = \frac{\nu_e^+[Na^+_{(aq)}]\nu_e^-[Cl^-_{(aq)}]}{[NaCl_{cr}]} \ \frac{\nu_w^+[H_3O^+_{(aq)}]\nu_w^-[OH^-_{(aq)}]}{[H_2O_{(aq)}]}$$

The reviewer is correct in that equilibrium constants are usually expressed in terms of their product rather than their sum, which is expressed by K2. K2 is simply another way of expressing the corrected version of K1. But eventually both are NOT needed to derive eqs. 19 - 23.

Reviewer 3: Equation (15) appears to equate solvent and solute activities to each other in saturated solutions.

Reply: Yes, but only with different exponents (and their signs). This should be noted as

well.

Reviewer 3: Solute activity coefficients are described as being functions of solubility, which is more or less a reversal of the true relation.

Reply: Yes, but only for the current paradigm. Why not, since we can measure more easily the solubility than the activity coefïňA̧cients?

Reviewer 3: Are solute and solvent activities related through the Gibbs-Duhem equation in this model?

Reply: They are related by the newly introduced stoichiometric constant of water, ν_w, whose usage/introduction, or simply its presence, needs to be understood first in order to understand the approach used in EQSAM3.

Reviewer 3: 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.

Reply: Again, it seems as if ML2007 did not explain their approach in sufficient detail. ML tried to explain this, in particular they have spent the entire section at page 3186, i.e. sect 5.3 Osmosis. One can follow the debate around the work of Heyrovska and others, that it is for some still not understood – for more than hundred years (!) it has not been understood that one can use/assume a single (effective) constant over the entire activity range, instead of using complicated solution dependent activity coefficients. What makes ML07 distinct from Heyrovska (1989) and others is that ML2007 have now introduced the stoichiometric constant of water, ν_w, while both approaches can obviously cope with only a single constant (by following Arrhenius' theory of partial dissociation), while other approaches obviously can not. But that ML can make a big difference for the numerical applications (in terms of complexity and speed), especially it makes the application feasible in our 3D modeling of atmospheric chemistry.

Reviewer 3: 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.

Reply: It could also be that the approach of ML2007 is not understood for other reasons. Otherwise one would try to accept this paradigm shift and rather judge the applicability and correctness of the approach by the various model applications which will follow and which eventually will tell us whether the approach introduced by ML07 is nonsense or not.

Reviewer 3: There are various general claims throughout the ms that make me fear the latter. These include, for example, statements that the Kelvin effect and Köhler 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."

Reply: As ML mentioned in their Open Discussion comments, the claims in ML2007 regarding the Kelvin effect do not affect the current model inter-comparison.

Reviewer 3: 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.

Reply: EQSAM3 is indeed not a traditional thermodynamic model, since it is not based upon traditional thermodynamic principles as stated in ML07. We will therefore refrain from calling EQSAM3 a "thermodynamics model" as stated above. But it is not true that it cannot be relied upon, as shown by the results of this work and the additional model comparsion with E-AIM and ISORROPIA2 (included in the ML2009 reply to Lescroart

and colleagues, which complements the present reply).

Reviewer 3: 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.

Reply: The altered manuscript will include comparisons with the AIM model (and this has also been shown in the ML reply to Lescroart). Moreover, as stated above, our goal with the present paper was to put the model through this intercomparison in order to expose any flaws, if present in ML07. We think the paper has done that. The model and its basic approach is already being used. Thus this intercomparison is necessary and useful.

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