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

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The title “A comparison of water uptake by aerosols using two thermodynamic models” of the paper proposed by L. Xu et al., and the related abstract clearly state that the authors compare (simulation) results based on what they regard as two thermodynamic models, EQUISOLV II and EQSAM3 the latter being presented (page 9556, line 3) as the first solubility-based thermodynamic gas/aerosol equilibrium model. On top of page 9554, EQSAM3 is cited among a dozen of thermodynamic equilibrium models and referred to as such through the whole paper.

Our point is that EQSAM3 is not a thermodynamic model and hence that any comparison with real thermodynamic models cannot be relevant. Xu et al. state that “EQSAM3 is based on a new analytical concept” (page 9554, line20) described in Metzger, S. and Lelieveld, J.: Reformulating atmospheric aerosol thermodynamics and hygroscopic growth into fog, haze and clouds, Atmos. Chem. Phys., 7, 2007 (`http://www.atmos-chem-phys.net/7/3163/2007/acp-7-3163-2007.pdf`).

However, no clear and explicit description of any (thermodynamic) model can be found in that paper. Moreover, it contains so many mistakes that one of the reviewers (A. Wexler, `http://mae.ucdavis.edu/wexler`) wrote that it would be hard to list them all. Our evaluation is that this is still the case in the published version. Some of these errors are fundamental and are killing the logic and the scientific soundness of the entire development. As these are key to the presently discussed paper, we will describe some of the errors in the development of the EQSAM3 model (Metzger, S. and Lelieveld, J., 2007).

As an example, the pivot equation (19):

$$\nu_w = -1 + \log\left(\frac{2}{\nu_e} \times 1000 \cdot w_s\right)$$

- displays three variables: w_s (solubility), ν_w and ν_e the latter being the newly introduced stoichiometric coefficients defined in a chemical equation (R1). Besides being of an unusual format, this equation (R1) cannot be correct because the authors are confusing hydration and hydrolysis:

$$n_s^{\mathrm{NaCl(cr)}} + n_w^{\mathrm{H_2O(aq)}} \leftrightarrow \nu_e^+ n_s^{\mathrm{Na^+_{(aq)}}} + \nu_e^- n_s^{\mathrm{Cl^-_{(aq)}}} + \nu_w^+ n_w^{\mathrm{H_3O^+_{(aq)}}} + \nu_w^- n_w^{\mathrm{OH^-_{(aq)}}}$$

- Equation 19 cannot be obtained from its introducing paragraph and the previous equations. For instance, where does the (decimal) logarithmic function come from ?

- according to (18d) the argument of the log function is not dimensionless, it is a mass:

$$\tilde{n}_w M_w = 1000 \times w_s \text{ where } \tilde{n}_w = n_{w,0} - n_w \text{ and } n_{w,0} = 55,51[\text{mol}]$$

- for symmetry reasons we would expect ν_w and ν_e to be either both inside or both outside the log function (or even both in and out) but not one inside and the other not,
- if ever, ν_e should multiply w_s, not divide.

Further, referring to fig. 1a and to equations (2) and (3)

$$p_{w,0}^{(g)} \cdot V^{(g)} = n_{w,0}^{(g)} \cdot RT$$

$$\Pi_{w,0} \cdot V^{(aq)} = n_{w,0} \cdot RT$$

and to the statement (2.1.2 – 7th line) :

$$p_{w,0}^{(g)} = \Pi_{w,0}$$

we can easily calculate:

$$\frac{n_{w,0}^{(g)}}{V^{(g)}} = \frac{n_{w,0}}{V^{(aq)}}$$

equalizing vapour density and liquid water density !

So, because of these mistakes, misconceptions and confusions, and many others not reported here but available on `www.climate.be/users/marbaix/acpd-Xu-Metzger.pdf`, we are convinced that EQSAM3 cannot be considered as a thermodynamic model or as based on such a model, and therefore we think it is misleading to compare it with a real and recognized model (EQUISOLV II).

In their paper, Xu et al. write that “the prediction of the portioning of the volatile inorganic aerosol components between the gas and aerosol phases (. . .) and the aerosol associated water is of great importance in the development of climate models (page 9554, line 25). Furthermore, they state that “Accurate methods for predicting atmospheric aerosol composition must be developed in order to better quantify and to understand the underlying physical and chemical processes.” (page 9552, line26). Thus, because there are no sound physical and chemical processes underlying the core equations of EQSAM3, the authors should avoid recommending incorporating it “into global aerosol models to solve the thermodynamics under chemical equilibrium conditions” (page 9578, lines 2 to 5). “Comparable results” and “high computational efficiency” (page 9578, lines 2 and 3) do not validate the highly questionable underlying theoretical approach of EQSAM3.

A bad model can provide apparently reasonable numbers when errors compensate each other or if tuning has taken place. But that model would produce irrelevant results under different conditions. We therefore strongly recommend that the authors (Xu et al.) do not take for granted the thermodynamic basis of the EQSAM3 model, and question fundamentally the solidity of its approach, in the light of our full comments and those of Wexler. Publishing the Xu et al. paper without that further analysis would mislead the community by giving credence to the EQSAM3 approach.

R. Lescroart and Jean-Pascal van Ypersele, 10/06/2009