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Comment

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

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We thank R. Lescroart and Prof Jean-Pascal van Ypersele for their interactive comment on “A comparison of water uptake by aerosols using two thermodynamic models” by L. Xu et al.

We believe that their major concerns arise from misunderstandings of our work and the available literature, so we would like to take the chance for clarification.

R. Lescroart:

“As an example, the pivot equation (19), 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).

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Reply:

Only ν_w is newly introduced.

On page 3167 of the EQSAM3 introductory paper, Metzger and Lelieveld (2007), (<http://www.atmos-chem-phys.net/7/3163/2007/acp-7-3163-2007.html>), hereafter referred to ML07, we wrote:

"We therefore introduce a stoichiometric coefficient $\nu_w = \nu_+ + \nu_-$ for the solvent (water) to account for the number of moles of solvent (water) needed for solvation (hydration) and solute dissociation.

R. Lescroart:

"(R1) cannot be correct because the authors are confusing hydration and hydrolysis"

Reply:

We refer to "solvation (hydration)" as stated above (i.e. page 3167).

For clarification, referring to:

<http://en.wikipedia.org/wiki/Solvation>

<http://en.wikipedia.org/wiki/Hydration>

<http://en.wikipedia.org/wiki/Hydrolysis>

By an IUPAC definition, solvation is an interaction of a solute with the solvent, which leads to stabilization of the solute species in the solution.

Solvation is, in concept, distinct from dissolution and solubility. Dissolution is a kinetic process, and is quantified by its rate. Solubility quantifies the dynamic equilibrium state achieved when the rate of dissolution equals the rate of precipitation.

Hydration differs from hydrolysis in that hydrolysis cleaves the non-water component in two. Hydration leaves the non-water component intact.

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The most common hydrolysis occurs when a salt of a weak acid or weak base (or both) is dissolved in water. Water autoionizes into negative hydroxyl ions and hydrogen ions. The salt breaks down into positive and negative ions. For example, sodium acetate dissociates in water into sodium and acetate ions. Sodium ions react very little with hydroxyl ions whereas acetate ions combine with hydrogen ions to produce neutral acetic acid, and the net result is a relative excess of hydroxyl ions, causing a basic solution.

Our νw -approach simply tries to account for the total water mass involved in any of the above processes where a (salt) solute dissolves. It takes into account solvation (hydration), while it is based on the solute solubility. So it could be referred to a combination of different approaches.

R. Lescroart:

"Equation 19 cannot be obtained from its introducing paragraph and the previous equations. According to (18d) the argument of the log function is not dimensionless, it is a mass"

Reply:

The argument of the log function, $1000 w_s$, is by itself dimensionless:

w_s denotes the dimensionless solute massfraction and the factor 1000 is a (dimensionless) number.

The log function should be considered in analogy to the pH calculation, as the charge transfer of a neutralization reaction in water can be expressed in terms of equivalent moles of H^+ (H_3O^+).

R. Lescroart:

"Further, referring to fig. 1a and to equations (2) and (3), ..., we can easily calculate, ..., equalizing vapour density and liquid water density"

Reply:

Equations (2) and (3) are valid for thermodynamic equilibrium and have been utilized already by van't Hoff and Ostwald about half a decade after Pfeffer's investigations to interpret the osmotic pressure (van 't Hoff, 1887), as stated at p3167 of ML07.

Caution, the equations refer only to the amount of water that needs to be exchanged to reach equilibrium, i.e. the case when above the surface evaporation of water molecules balances the condensation of water molecules!

Final relpy:

Even if some aspects of ML07 might have been explained more clearly, one should not forget or play down that this approach, the newly introduced stoichiometric coefficient for water, allows for the first time an analytical while rigorous and computationally very efficient calculation of important thermodynamic properties, such as the activity of binary or mixed solutions, from which the associated water content of various solutes containing either single or multiple charged ions can be derived. This has been clearly demonstarted in both, ML07 and the current work by L. Xu et al.

So we think there is no reason to state that "EQSAM3 cannot be considered as a thermodynamic model or as based on such a model", or that it "is misleading to compare it with a real and recognized model (EQUISOLV II)".

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

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