

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

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**S. Metzger and J. Lelieveld**

Reply to some critical remarks by Lescroart and van Ypersele, including some remarks in a pdf document that is circulated with the additional co-authors Marbaix and Ferrone outside the regular reviewing process (rather disagreeably).

**Lescroart et al.:**

Our point is that EQSAM3 is not a thermodynamic model and hence that any comparison with real thermodynamic models cannot be relevant.

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**Reply:**

We appreciate the effort of re-reviewing the ML07 paper

(<http://www.atmos-chem-phys.net/7/3163/2007/acp-7-3163-2007.html>)

and would agree that theoretical concepts should be open for discussion. However, we consider the above remark by Lescroart et al. to be a post-hoc fallacy and do not agree that the comparison of EQSAM3 with EQUISOLV II is not relevant. The present manuscript by Xu et al refers to EQSAM3, which applies the equations 19-23 of ML07. In ML07 these equations are used to e.g. successfully predict the relative humidity of deliquescence (RHD) and the aerosol associated water mass. The agreement with observations and other models is remarkable and is unlikely to be coincidental, especially if the theoretical concept would be wrong.

To corroborate that the results of EQSAM3 are unlikely to be coincidental we include an additional inter-comparison with the reputed models ISORROPIA2 (<http://nenes.eas.gatech.edu/ISORROPIA/>) and E-AIM, the latter generally regarded as a reference model (<http://www.aim.env.uea.ac.uk/aim/aim.php>). Results are shown for the aerosol water uptake, being a critical and highly relevant parameter. Four cases are shown, i.e. two single solutions for pure NaCl and water (Fig 1), pure  $\text{NH}_4\text{NO}_3$  and water (Fig 2), and two mixed solutions for NaCl and  $\text{NaNO}_3$  and water (Fig 3), as well as  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NH}_4\text{NO}_3$  and water (Fig 4). All three models predict nearly the same water uptake over a wide range of RH, despite the very different concepts and numerical treatment. Again we emphasize that EQSAM3 only requires the solute solubility as input (either measured or calculated) from which all relevant thermodynamic properties are consistently derived, including the RHD, the water activity and the single or mixed solution concentration, or the activity coefficient for  $\text{NH}_4\text{NO}_3$  (for the other cases activity coefficients are not needed).

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Note that most models employ various data for the RHD, water activity, equilibrium constants, etc., and are using activity coefficients for all compounds. In fact, all methods are semi-empirical in nature because none computes all parameters based on first principles. In this respect, EQSAM3 is no exception, although the empirical data needed is really minimal; again, EQSAM3 only requires the solute solubility (independent whether these are measurements or calculations).

Nevertheless, we would agree that our  $v_w$ -approach could be called a parameterization or a semi-empirical approach, similar to the activity coefficients methods used in thermodynamic models. All other parameters, however, are directly derived from  $v_w$  and not parameterized in EQSAM3.

In turn,  $v_w$  is directly calculated from the solute solubility by eq. 19. Independently whether one accepts eq. 19 as explicitly derived, assumed or parameterized, its use in eq. 20 is key to the simplifications brought forward in ML07. It should be stressed that Eq. 19 is not explicitly derived in ML07, and as such we accept some of the debate about ML07, where this could have been stated more clearly.

But independently whether eq. 19 is (semi-)empirical or derived, it does not make a difference for its successful application. Our point is that introducing and applying a stoichiometric constant for water,  $v_w$ , clearly has the advantage that it allows various simplifications as brought forward by ML07.

To underpin that the agreement of EQSAM3 with other models is not coincidental, we emphasize that the src-code is freely available (for non-commercial applications), so that our calculations can be tested and extended to other conditions. Furthermore we

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are open for additional suggestions to be included into this ACPD discussion. And we would be thankful for constructive comments that help improve the code and supports further improvements of EQSAM3.

What would be most relevant for reviewing the Xu et al. manuscript is that models are judged upon their predictive capability. Therefore it is important to disentangle the concept discussion from the application in the present manuscript by Xu et al. We propose that Lescroart et al. (and Referee #3 and R. Zaveri) consider the testing of eqs. 19-23, being at the core of EQSAM3, which is done in Xu et al.

We furthermore suggest decoupling the EQSAM3 application by Xu et al. from the thermodynamic principles questioned by Referee #3, who includes a discussion about 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 present review.

Below we nevertheless reply to the partly discourteous comments by Lescroart et al. to explain the concepts of ML07, hoping to defuse the controversy:

**Lescroart et al.:**

Fundamental scientific problems:

1. Confusion between osmotic pressure and vapour pressure (1)  
... equalizing vapour density and liquid water density!
2. Confusion between osmotic pressure and vapour pressure (2)  
...So, osmotic pressures and vapour pressures (in the given circumstances) are just not comparable.

**Reply:**

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Equations (2) and (3) refer to the gas-solution analogy which is widely used and valid at thermodynamic equilibrium; it has already been used 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 on p3167 of ML07.

Caution: there might be some confusion as we do refer here only to the amount of water that is needed for solvation / hydration / dissociation, etc. and hence only to the change in the partial pressure of water, which, in equilibrium, must be identical to the change in the partial osmotic pressure of water. And this change defines the water uptake at the required equilibrium condition. Once a solute is in equilibrium with water, the solution is saturated. Saturation describes the co-existence of liquid and gas phase, including the solid phase for a (soluble) solute (co-equilibrium wrt precipitation and dissolution of the solute), and occurs along the lines of a phase diagram. For water, the vapor saturation occurs between the triple point and the boiling point, being equally valid for partial pressures, including a change in the partial pressure of water, to which we refer in ML07. So equations (2) and (3) are valid.

The notation in the sentence above eq.(3) on p3166, sec 2.1.2, refers to changes ( $\Delta$ ) rather than to the absolute values according to the introduction section 2.1.1 (same page just left column). Also, eq. (4), next page, on which everything for the lab is build on, is based on changes ( $\Delta$ ). Eq.(3) is not needed and only shown as an example for the gas-solution analogy.

### **Lescroart et al.:**

#### 3. Confusion between osmotic pressure and chemical potential.

If we refer to osmotic pressure as the pressure generated across a semi-permeable membrane between two solutions with different concentrations, then the very concept of osmotic pressure of water  $\Pi_w$  (p. 3166 -9th line) is nonsense.

We think osmotic pressure here stands for escaping tendency of the water molecules

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which means that Swen Metzger is mistaking osmotic pressure for chemical potential (see fig. 1a).

**Reply:**

We are referring to the partial pressure of water, i.e. the partial pressure of water in either the gas or liquid phase of a mixed solution (s. section 2.1.1, p3166). In this case, an osmotic pressure of water is useful and leads to meaningful and correct results (e.g. see derived RHD values; comparing tables 1 and 2 of ML07).

**Lescroart et al.:**

4. Confusion between hydration and hydrolysis.

**Reply:**

By the 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 determined by its rate. Solubility represents the dynamic equilibrium state achieved when the rate of dissolution equals the rate of precipitation to form the solid.

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

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, in water sodium acetate dissociates into sodium and acetate ions. Sodium ions hardly react with hydroxyl ions whereas acetate ions combine with hydrogen ions to produce neutral

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acetic acid, and the net result is a relative excess of hydroxyl ions, causing a basic solution.

Our  $v_w$ -approach aims 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) as well as hydrolysis, and is based on the solute solubility. So it could be referred to as a combination of different approaches which might give rise to controversy. This has been summarized by R(1), where  $v_{-w}^+$  and  $v_{-w}^-$  refer to the stoichiometric involvement of water, whether it is participating in hydrolysis or hydration, and which hence appears unusual but is nevertheless useful and correct.

#### Lescroart et al.:

5. Confusion between  $\Delta E = 0$  and  $dG = 0$  as an equilibrium condition.

First, even if the  $p \cdot V$  and  $\Pi \cdot V$  terms (see equations (1) to (3)) have the dimension of energy, they are not, in our opinion, the expressions of the system's energy.

Further, even with  $E = \Pi \cdot V(aq)$  one cannot write:

$$\Delta E = \Delta \Pi \cdot \Delta V(aq) = 0 \quad (7)$$

By the way, (7) gives rise to (9):

$$v_e \Delta n_s = -v_w \Delta n_w \quad (9)$$

where, according to Swen Metzger, the term on the rhs expresses the amount of water required for the hydration of  $\Delta n_s$  moles of solute (3.4 – 3rd line). Not surprisingly this is again nonsense as we will see below.

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**Reply:**

Again, we are not referring to the system energy but, as also stated in ML07, to the partial energies and volumes that correspond to the amount of water that is needed to reach equilibrium (due to solvation/hydration/dissociation).

Eq. (9) is not nonsense, as we are referring to a change of water. Depending on what is taken as a reference, i.e. either the ideal solution = pure water (right compartment of Fig. 1 of ML07, or the mixed solution where a solute is added to water (left compartment). To hydrate a solute (latter case) water has to be taken from the right compartment, so that the amount of pure water decreases, for example. Of course this is only used for illustration, similar to the membrane, which does not exist in the real atmospheric aerosol. Nevertheless, the computation remains unchanged for atmospheric conditions and is applicable, as outlined in ML07.

Btw. if eqn. (9) or other parts criticized here would be nonsense, the main eqs. (20-22) which rely on eq.(9) would not yield results that can correctly reproduce both observational data and other model calculations (besides the RHDs) for e.g. the single solute molalities or the aerosol water mass, as extensively shown in supplement of ML07 and in the figures 1-4 of this reply.

**Lescroart et al.:**

Formal (but not less important) problems.

1. Throughout the paper, to one mole of solute correspond different numbers of moles of water :

p. 3172 - 5th line :  $v_w$  moles of water

(R1)  $v_w n_w / n_s$  moles of water

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p. 3169 - 23rd line :  $-v_w \Delta n_w / v_e \Delta n_s$  moles of water

3.4 - equation (9) :  $-v_w \Delta n_w / v_e \Delta n_s$  moles of water with  $\Delta n_w < 0$  !

**Reply:**

This is not correct. (R1) is not correctly interpreted and the latter two of the above statements are the same and referring to the total amount of water that drives hydration. On p. 3172 - 5th line, we refer to the case to reach electroneutrality.

Our  $v_w$ -approach aims 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) as well as hydrolysis, and is based on the solute solubility. So it could be referred to as a combination of different approaches, which might give rise to controversy. This has been summarized by R(1), where  $v_w^+$  and  $v_w^-$  refer to the stoichiometric involvement of water, whether it is participating in hydrolysis or hydration, and which hence appears unusual but is nevertheless useful and correct (see above).

**Lescroart et al.:**

2. Equation (9) :  $\Delta n_w < 0$  for  $\Delta n_s > 0$ . If some solute is added to the solution, there should be a further water uptake (until the water activity again equals RH) which means that for  $\Delta n_s > 0$ , we necessarily have  $\Delta n_w > 0$

**Reply:**

The above interpretation is not correct because  $\Delta n_w$  here refers to the change in the number of moles of water with respect to the ideal solution = pure water (right compartment of Fig. 1 of ML07; in the mixed solution a solute is added to water = left compartment). To hydrate a solute water has to be taken from the right compartment, so that the amount of pure water decreases, for example. Again, of course this

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is only used for illustration, similar to the membrane, which does not exist in the real atmospheric aerosol. Nevertheless, the computation remains unchanged for atmospheric conditions and is applicable, as outlined in ML07. Note. The fact that the sign is negative indicates a phase changes and is considered in the exponent (eq.14).

**Lescroart et al.:**

According to the values of table 1.a for NaCl ( $v_w = 1,423$ ):  $v_w \Delta n_w > \Delta n_w$  and the amount of water required for hydration is superior to the amount of water that has been taken up ... (see also (R1)).

**Reply:**

This equation and R1 are not interpreted correctly (same as above); both stoichiometric constants need to be considered, the one for water and the effective one for the solute as described in ML07.

**Lescroart et al.:**

4. Equation (20) (pivot equation): from what is written before, it is easy to derive this equation but without the exponent  $v_w/v_e$ . Where does it come from?

**Reply:** Equilibrium reactions are written with their stoichiometric constant as exponent; see e.g. eq. (12) of the supplement of ML07 which summarizes the standard definitions and relevant equations for chemical equilibrium.

Introducing the stoichiometric constant for water, both the solute concentration and the water activity have to be expressed in terms of their stoichiometric constant as an exponent. Upon rearranging of the exponents to one side yields eq. (20).

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**Lescroart et al.:**

The case of equation (19) (pivot equation) :

- Besides talking about electroneutrality (?) and mixing up once again hydration and hydrolysis, the paragraph introducing equation (19) explains just nothing.
- Where does the (decimal) log function come from ?
- We would expect  $v_w$  and  $v_e$  both in or both outside the log function but not one in and the other not.
- $v_e$  should multiply  $w_s$ , not divide.
- According to (18d) the argument of the log function is not dimensionless, it's a mass.
- There are no typos, we've been able to check the equation because it calculates values from table 1a.

**Reply:** The argument of the log function,  $1000 w_s$ , is dimensionless:  $w_s$  denotes the dimensionless solute mass fraction and the factor 1000 is dimensionless. The value of 1000 has units of g in ML07. It is common to use values with units within the log term for aerosol size distributions, but it is understood that one is dividing by the value of 1 with the same unit. That is what we are assuming here. A similar assumption is made when one defines the pH of a solution.

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  $H^+$  ( $H_3O^+$ ).

In summary, the remarks by Lescroart et al. indicate that some of the arguments in ML07 have not been understood, but not that they are incorrect. Some of the argumentation may indeed be unconventional, however, if interpreted in the manner meant by ML07, mathematically correct. Much of the controversy addressed by Lescroart et al is about the definitions of solvation, hydration, hydrolysis, osmosis, chemical potential etc, while arguments to support that EQSAM3 is not a useful model

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**Fig. 1.** Aerosol water as function of RH for single solution NaCl.

**Fig. 2.** Aerosol water as function of RH for single solution  $\text{NH}_4\text{NO}_3$ .

are lacking. It would be more constructive to study why eqs. 19–20 by ML07 are successful, especially because they have been derived unconventionally.

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**Fig. 3.** Aerosol water as function of RH for mixed solution NaCl-NaNO<sub>3</sub>.

**Fig. 4.** Aerosol water as function of RH for mixed solution (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>-NH<sub>4</sub>NO<sub>3</sub>.

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