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Comment

## ***Interactive comment on* “Derivation of the stoichiometric coefficient of water ( $\nu_w$ ) to account for water uptake by atmospheric aerosols” by S. Metzger et al.**

**S. Metzger et al.**

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### **1 General reply**

We thank R. Lescoart for his detailed review. We believe, however, that the negative argumentation and recommendation to reject the manuscript and the associated application paper of Xu et al. (<http://www.atmos-chem-phys-discuss.net/9/9551/2009/>) are unfounded.

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- The  $v_w$  concept (ML07) can be applied in atmospheric modeling studies, as shown by this work, the accompanying application paper of Xu et al. (2009) and ML07, independently whether or not  $v_w$  is derived from first principles. However, we concur that our attempts to provide a physical explanation for our concept have been unsuccessful thus far. Therefore, in our re-submission of the manuscript we will abandon it (probably providing it separately) and concentrate on a parameterization of gas-aerosol partitioning, including the uptake of water, and discuss the differences with alternative methods. In fact, the introduction of a new empirical coefficient should not preclude its use in a parameterization model such as EQSAM3 for which we show that the results fit measurements and the results of the reference model E-AIM for the defined range of atmospheric conditions (demonstrated by e.g. Figure 2).
- Our empirical approach does not fundamentally differ from other concepts in this field (e.g. Raoult's law ( $x$ ), van't Hoff factor ( $i$ ), osmotic coefficients ( $\phi$ ), activity coefficients ( $\gamma$ ), effective hygroscopicity parameter ( $\kappa$ ), etc.), which have been introduced to correct for solution non-idealities, without providing an explanation based on first principles of physical chemistry. We had hoped to present a detailed derivation of  $v_w$  to answer the open questions; however, we will pursue this independently from the parameterization description and we welcome further discussions.
- We will thus revise the derivation paper and make the following changes / additions to help resolve the debate. To make our concept clearer, we will:
  - (i) add new sections that put our concept in context to other (including Köhler theory and various water activity representations), and present equations that relate  $v_w$  to  $x$ ,  $\gamma$ ,  $\phi$ ,  $i$ ,  $\kappa$  and to the mass equivalent growth factor  $g_m(RH)$  and deliquescence humidity (RHD) of single and mixed salt solutes;
  - (ii) include tables of additional results of  $v_w$  based calculations of  $g_m(RH)$ ,

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$\phi(RH)$  and  $\kappa(RH)$  in a comparison with E-AIM and H-TDMA measurements.

(iii) improve the key equation of single solute molality to account for a better  $g_m$  at RH > 95% (at lower RH the results remain unchanged);

(v) add a further mathematical development of a single parameter parameterization that could be used instead and easily determined from reference data, e.g. E-AIM  $\phi$  or RHD predictions,  $\kappa$  H-TDMA measurements, etc.

(iv) further improve the derivation of  $v_w$  (probably providing it separately);

- Despite the various changes / additions, the new concept of equations for  $v_w$  in ML07 remain unchanged but will be better explained.
- Note that the main advantage in using  $v_w$  clearly is its simplicity – the use of effective coefficients for solute and solvent allows one to directly solve a set of analytical equations rather than performing computationally expensive minimization of the Gibbs free energy.
- This simplicity and accuracy can be easily verified with the example program to calculate the RHD and hygroscopic growth of NaCl from RHD up to conditions close to those of water vapor saturation, which can be easily extended to other compounds and which is provided in the supplement of this reply.

## 2 Point-to-point reply

Unfortunately, most arguments are based on a mis-interpretation of our work, while reference to a book of Dill and Bromberg is given, who explain osmotic pressure using traditional chemical potentials, which is fine but not useful for the present discussion. Even if there would be aspects in our derivation that remain to be clarified or improved,  $v_w$  may be conceived as an empirical coefficient, on the same level as many other

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relationships used in reference models (including E-AIM). In contrast to many other approaches, application of this concept has the advantage of not requiring additional correction factors (e.g. osmotic coefficients, van't Hoff factors, activity coefficients). The use of  $v_w$  and  $v_e$  are correction factors – the main difference is that they not only linearly correct the mole fraction or molality. Instead, they appear also in the exponent of the form  $a x^a$  (see e.g. Eq. (A10) for the RHD calculation), so that indeed only one constant correction factor (i.e. the ratio  $v_w/v_e$ ) is sufficient to emend the mole fraction or molality for the whole range of water activity ( $a_w$ ) or relative humidity (RH), while all other approaches actually require for each  $a_w$  or RH step an individual correction factor. Thus, being able to predict the water activity over the whole range of RH with only one constant factor is especially important for the application in large-scale atmospheric chemistry models, independently whether this parameter has been derived from first principles or simply mathematical fitted to reference data.

Nevertheless, some aspects were correctly identified by the reviewer as unclear and misleading, for which we are grateful. We will improve this in the revised manuscript and hope to have clarified and resolved the unclear aspects mentioned in this review. A detailed point-to-point response is given below – see also the additional explanations in the revised manuscript.

- *Lescroart: The authors claim to have derived the effective stoichiometric coefficient of water  $v_w$  from first principles. This is not true.*

- Reply:

In this work, we focus on the derivation of the effective stoichiometric coefficient of water  $v_w$ , which was introduced by ML07. One can argue about "first principles" in thermodynamics, and we will withdraw this statement, although we will present a detailed analogy to the description of osmosis.  $v_w$  is derived from the solute solubility by defining and solving the fundamental equations of the associated

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changes in energy (of the solution and of pure water), i.e. the work done by the two compartments due to the volume changes,  $\Delta V_{\text{sol}}$  and  $\Delta V_{\text{w}}^{\circ}$  against the associated pressure changes  $\Delta P_{\text{sol}}$  and  $\Delta P_{\text{w}}$ , at temperature  $T$  for a solution which saturates when equilibrium is reached. This will be clarified.

- *Lescroart: On page 8173, line 23, they introduce artificially, without scientific explanation, an arbitrary scaling factor featuring  $v_{\text{w}}$ . This is how  $v_{\text{w}}$  comes into final play. There is no derivation from whatever scientific principles at all.*

- Reply:

ML07 have introduced  $v_{\text{w}}$  for the first time. In physical chemistry and thermodynamics such a parameter has not yet been introduced, and we fail to see why it would not be allowed to do so, especially since we provide compelling evidence showing that the concept works. This will be clarified in the revised manuscript.

The scientific explanation is given one page earlier (i.e. page 8172, line 20-24.).

- *Lescroart: In my opinion, this misleading procedure alone is enough to reject the paper.*

- Reply:

If misleading, why do the results show excellent agreement with various deliquescence measurements, or with water uptake calculations of reference thermodynamic models for binary and even mixed solutions? Providing a means to perform such calculations can hardly be misleading. If empirical coefficients and assumptions such as the empirically derived ZSR relation are allowed, why not a new coefficient with advantages?

- *Lescroart: But in the same line, a fundamental mathematical error appears. Once corrected, the final expression of  $v_{\text{w}}$  is totally different and yields very different values.*

- Reply: If interpreted correctly (see reply further below), there is no fundamental mathematical error. Hence, the results do not change, nor other final expression of  $v_w$  can be presented. This will be clarified in the revised manuscript.
- *Lescroart: But, in order to show that these are not mere accidents, I will display here a full list of the many errors, confusions and misunderstandings I've detected. I'm aware that the list could be incomplete, for the writing seems sometimes confusing and ambiguous and makes it very difficult and even meaningless to try to detect all the errors and contradictions.*
- Reply: This statement is tendentious, as shown by our detailed point-to-point reply below.
- *Lescroart: page 8167 : lines 16 and 18 : two very different values for the same constant  $m_w^o = 1 \text{ kg}$  and  $m_w^o = 162.33 \text{ g}$  (Metzger et al. 2007 (ML07)).*
- Reply:  
The two different values are clearly defined on page 8167 line 16 and 17 and refer to two different cases, which are both applicable using the same constant  $m_w^o$ : Case a) with a reference mass of water 1 [kg] and a corresponding mass of solute of 0.36 [kg], and case b) of with a reference mass of water 162.33 [g] and corresponding mass of solute of 58.44 [g]; both for NaCl and w.r.t saturation.
- *Lescroart: page 8167 : lines 17 and 18 : contradiction in values of  $n_{\text{sat}}$  : "1" on line 17, "6.16" on line 18.*
- Reply: See above.
- *Lescroart: page 8167 : line 19 :  $n_s^{\text{sat}}$  is not well defined : one should add "in 1 kg of water".*

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- Reply:

$n_s^{\text{sat}}$  denotes the number of moles of solute at saturation and is correctly defined on line 19 considering what was written on line 16-18 (all page 8167). There is nothing wrong with the example or values given. However, we will add a note in the revised manuscript.

- *Lescroart: page 8167 : lines 20 to 23 : it is shown nowhere in the paper that  $v_w$  should have the same value in saturated and non saturated solutions.*

- Reply:

On page page 8169, line 26, we mention the gas-solution analogy to which we refer by Eq. 8 on page 8173. From the rhs of Eq. 8, i.e. from the ratio of moles of solute and water (needed to yield a saturated solution, thus considering absolute changes) it becomes clear that there is no dependency on the water reservoir such as the right compartment of Fig. 1, or whether the water molecules condense from the gas phase, or are provided from elsewhere. To make this even clearer, we will add a note in the revised manuscript.

- *Lescroart: Before starting the review of the next pages, I would like to make clear some basic facts about osmosis (see fig.1 (Metzger et al. 2010) and also e.g. "Molecular Driving Forces" by K. A Dill and S. Bromberg, 2003):*

- Reply:

1. These basic facts are not in contradiction to what we have summarized here (each point will be addressed below).
2. Dill and Bromberg explain osmotic pressure using chemical potentials (which is not appropriate for the present discussion).

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- *Lescroart: just adding NaCl to water (not considering osmose yet) only slightly increases its volume : volume (water + NaCl) < (volume water) + (volume NaCl), as can be easily checked by considering the density of saline solutions;*

- Reply:

Starting on page 8169 with line 1 (ending on line 17 of 8170), a detailed description is given of the associated volume changes, with a summary on page 8170, lines 3-15).

However, we omitted here any speculation about the magnitude of the different contribution to the total volume changes, as this is redundant for our derivation of  $v_w$ . The final result, i.e. Eq. (10c-f) shows that  $v_w$  is merely a function of solute solubility (besides the effective stoichiometric coefficient of solute,  $v_e$ ), and by this independent of the solute concentration. We will add a note in the revised manuscript to clarify.

- *Lescroart: hence, the level in the left pipe would rise only slightly due to this process;*

- Reply:

Independently whether the level in the left pipe would rise only "slightly", this does not matter for the same reason given in the previous reply, i.e.  $v_w$  is merely a function of solute solubility (besides  $v_e$ ), and by this independent of the solute concentration.

- *Lescroart: also, the ionisation of salt molecules (and re-arrangement of some water molecules around them) doesn't in itself increase the volume of the solution;*

- Reply:



The degree of ionisation of salt molecules (and re-arrangement of some water molecules around them) is not relevant here, for the same reason given in the previous reply.  $v_w$  is merely a function of solute solubility, which implicitly accounts for the degree of ionisation (and re-arrangement of some water molecules around them), if an effective stoichiometric coefficient of solute,  $v_e$ , as done in this work, and in contrast to the textbook of K. A Dill and S. Bromberg, 2003.

- *Lescroart: but the hydration "consumes" (= fixes) a lot of water molecules, making less "free" water molecules available; and in the case of an osmosis set-up, the remaining free water molecules are not able to equilibrate migration through the membrane into the solution;*

- Reply:

While the reviewer uses qualitative expressions such as "a lot of water molecules" we instead have tried to quantify the water molecules associated with the dissolution of a salt compound, and e.g. "consumed" by processes such as hydration that drive the dissolution of the salt. This is explained on page 8169 (line 10-21).

- *Lescroart: hence, some net water flow invades the solution coming from the pure water compartment;*

- Reply:

This is explained on page 8169 (line 10-21) attempting to provide a quantitative expression (which substitute other correction factors, e.g. van't Hoff factor or activity coefficients). Unfortunately, this has not been recognized by the reviewer.

- *Lescroart: this process (osmosis) goes on until the level difference (sometimes huge) between the two pipes has become large enough to let a definite hydrostatic counter-pressure build up and equilibrate again the migration through the membrane;*

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- Reply: This is in accord with what we have stated at page 8169 (line 24-26).
- *Lescroart: hence the amount of water that migrates into the salt solution depends not only on the strength of hydration pull (nature of the solute and its concentration)*
- Reply:

It is evident that the hydration pull depends on the nature of the solute and its concentration. While in the literature the dependency on the nature of the solutes is usually neglected, and hence correction factors (e.g. van't Hoff factor or activity coefficients) are required (e.g. as in the textbook of K. A Dill and S. Bromberg, 2003), ML07 and this work introduce (use) the effective stoichiometric coefficient of water  $v_w$  to describe the amount water molecules associated with the dissolution of a salt compound, and e.g. effectively "consumed" by processes such as hydration that drive the dissolution of a salt compound, as  $v_w$  can be directly calculated from one single measurement value, i.e. the solute solubility (a quantity that is straightforward to measure in contrast to activity coefficients that need to be known for the whole range of water activities).
- *Lescroart: but also on the geometry of the device : the thinner the pipes, the less water has to migrate to install the necessary hydrostatic counter-pressure;*
- Reply:

The water molecules associated with the dissolution of a salt compound are - at equilibrium - independent of the geometry of the device. For the condition that the device (e.g. a capillary) affects the amount of water "consumed" by the solute, one would need to consider non-equilibrium cases that are not relevant for our derivation; the solubility is always measured at equilibrium.
- *Lescroart: Some of the comments that follow have to be viewed in the light of these "basic osmosis facts" (BOF).*

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- Reply:

There are no "basic osmosis facts" (BOF) adding information or in contradiction with our work. The comments that rely on the so-called "BOF" are thus not appropriate and helpful for a review of this work.

- *Lescroart: page 8168 : lines 12 and 13 : confusing and ambiguous use of the word "volume", here in moles, below in  $m^3$  without distinction.*

- Reply:

We state on page 8168 at lines 11-13: "Note that the stoichiometric coefficients (constants)  $v_w$  and  $v_s$  are dimensionless (scalars), and scale the number of moles of solute (and solvent) volume rather than e.g. adding (or subtracting) a number of moles or volume." This is important - not ambiguous - since we state in the next sentence:

"The masses of the solute and the solvent do not change during dissolution and dissociation; only volumes change because the number of moles changes due to partial or complete dissociation. It is this proportionality that enables us to derive  $v_w$ ."

We correctly use the SI-unit for volume.

- *Lescroart: page 8168 : lines 13 to 16 : as I read it, volume and number of moles are proportional; hence, here volume is in  $m^3$ , and more surprising : if (by ionization) the number of moles of particles increases, then the volume (in  $m^3$ ) should do also, proportionally. In contradiction with BOF.*

- Reply:

We state on page 8168 at lines 11-13: "The masses of the solute and the solvent do not change during dissolution and dissociation; only volumes change because the number of moles changes due to partial or complete dissociation. It is this

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proportionality that enables us to derive  $v_w$ ". There is no contradiction with such "BOF".

Three lines earlier (line 7-10) we explained:

"For instance, strong electrolytes such as  $\text{NaCl}_{(cr)}$  dissociate practically completely in water so that 1 mole of  $\text{NaCl}_{(cr)}$  yields 1 mole of  $\text{Na}_{(aq)}^+$  and 1 mole of  $\text{Cl}_{(aq)}^-$ , thus 1 mole of dry (crystalline) solute yields  $v_s=2$  moles ions of electrolyte in solution."

Thus, the volumes change (due to solute dissociation and "consumed" water) but not due to any further addition of moles (e.g. formed by chemical reactions) other than those that have already been added and dissolve. Note that hydration belongs to one chemical reaction such that affects the stoichiometry, so that the consumed water mass by the dissolved solute is accounted for (as summarized at page 8179, line 3-11).

- *Lescroart: page 8168 : line 18 : change of symbol : now the stoichiometric coefficient of water is written  $v_w^\pm$  in stead of  $v_w$  as previously.*

- Reply:

On page 8168 at lines 17-23 we clearly define  $v_w^\pm$  and explain the difference to  $v_w$ :

"Since many solutes do not dissociate completely, we will use in the following the symbol  $v_w$  to distinguish between the fraction of water that is associated with an undissociated solute, and  $v_w^\pm$  for an  $\pm$ -ion-pair, e.g. salt solute, that effectively dissociates into  $v_e^\pm$  ions, i.e.  $v_e^+$  cations and  $v_e^-$  anions, with  $v_e^\pm = v_e^+ + v_e^-$  and  $v_w^\pm = v_w^+ + v_w^-$ . Thus, the stoichiometric coefficient of water  $v_w^\pm$  expresses the fraction of water that is needed (e.g. for hydration) for each mole of solute to effectively dissociate into  $v_e^+$  cations and  $v_e^-$  anions."

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- *Lescroart: page 8168 : lines 26 to 28 : again the ambiguous use of "volume" : dissolution/dissociation (= increase of moles) and volume expansion, in  $m^3$  because linked to the "consequent hydrostatic counter-pressure".*

- Reply:

Again, as noted above, we state on page 8168 at lines 11-13: "Note that the stoichiometric coefficients (constants)  $v_w$  and  $v_s$  are dimensionless (scalars), and scale the number of moles of solute (and solvent) volume rather than e.g. adding (or subtracting) a number of moles or volume."

This is important - not ambiguous - as both, the solute mass that is added to water and the total water mass do not change during dissolution (as noted in our reply above, and clearly stated on page 8168 at lines 13-16).

- *Lescroart: page 8169 : lines 6 to 8 : do the authors really consider the volume expansion to be due to the ionization ?*

- Reply:

Yes, but only to distinguish the various volume contributions (see page 8170, lines 16-17 (and above), while the final equations (10c-10f) do not rely on any volume fraction, since  $v_w$  merely depends on the solute solubility (besides the effective stoichiometric coefficient of solute,  $v_e$ ). By this  $v_w$  is independent of the solute concentration, or volume fractions (ionization is accounted for by  $v_e$ , as mentioned several times before, e.g. page 8168, lines 16-23 or page 8169, lines 9-10).

- *Lescroart: page 8169 : line 9 : once again very ambiguous : there is no direct "volume expansion" due to the hydration water but instead the hydration process "pulls" some water through the membrane, the amount of which depends greatly on the geometry of the device (Pfeffer cell).*

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- Reply:

At equilibrium, the geometry of the device does not matter, while the "volume expansion" we consider here is due to the water consumed by dissolution/dissociation.

- *Lescroart: page 8169 : lines 10 to 15 : in contradiction with the BOF.*

- Reply:

There is no contradiction with BOF. The volume change is caused by the hydrating water molecules that drive the dissolution/dissociation.

We state on page 8169 at lines 10-15: The volume changes due to (1) the added mass of the solute, and (2) due to the amount of water required to dissolve and/or dissociate the solute, and bound to the solute ions as a hydration shell. This volume change causes a flow of water through the membrane (here from right to left) to compensate for the amount of water bound to the ions of the dissociating solute, until all solute mass is dissolved and the solution (left compartment) is saturated.

- *Lescroart: page 8169 : line 15 : in contradiction with the initial assumptions (page 8169, lines 1 and 2) : the solution in the left compartment is saturated from the beginning, before any osmotic migration.*

- Reply:

On page 8169 line 1 and 2 we only refer to the amount of water that is required to yield a saturated solution:

"Assume that both compartments are filled with a certain mass of pure water that corresponds to the saturation of 1 mole of solute"

while on page 8169, lines 5-9, we define the experiment:

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Thus, adding e.g. the pure (crystalline) solute  $\text{NaCl}_{(\text{cr})}$  to one (e.g. the left) compartment yields a concentration change (number of moles per volume) and a volume expansion, leading to two different height changes,  $\Delta h_{\text{sol}}$  and  $\Delta h_{\text{w}}^{\circ}$ , due to the number of  $v_{\text{e}}^{\pm}$  moles in which the solute effectively dissociates and due to  $v_{\text{w}}^{\pm}$ , the amount of water consumed during dissolution/dissociation.

So, we do NOT state that the "the solution in the left compartment is saturated from the beginning" as criticized by the reviewer. Thus, there is also no contradiction to what is written on line 15 of page 8169:

"This volume change causes a flow of water through the membrane (here from right to left) to compensate for the amount of water bound to the ions of the dissociating solute, until all solute mass is dissolved and the solution (left compartment) is saturated."

- *Lescroart: page 8169 : line 16 : there can be no saturation anymore, because some additional water has migrated into the solution.*

- Reply:

It is NOT correct that the "the solution in the left compartment is saturated from the beginning".

The reviewer should correctly refer to what is written!

- *Lescroart: page 8169 : line 21 : by definition, the osmotic pressure is measured by the hydrostatic counter-pressure needed to stop the migration flow through the membrane, it is equal to  $\Delta p_{\text{sol}} - \Delta p_{\text{w}}^{\circ}$  with  $\Delta p_{\text{w}}^{\circ} < 0$ ; hence notations  $\Pi_{\text{sol}}$  and  $\Pi_{\text{w}}$  are not suitable and I know no such contradictory thing as "the osmotic pressure of pure water" ( $\Pi_{\text{w}}$ ).*
- Reply:

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The osmotic pressure of pure water" ( $\Pi_w$ ) was introduced by ML07 for reasons explained on their page 3166, lines 13-21 to distinguish the contributions of solute and solvent to the total change in volume. And on page 8169 lines 16-21 we state:

"At saturation the system is in equilibrium again with maximum changes in the volume of both compartments,  $\Delta V_{\text{sol}}$  and  $\Delta V_w^{\circ}$ , respectively. Note that the volume of the right (pure water) compartment merely changes because of a flow of water through the membrane (osmotic drag). This flow stops when the hydrostatic counter pressures,  $\Delta p_{\text{sol}}$  and  $\Delta p_w^{\circ}$ , that build up due to the volume expansion compensate the osmotic pressures, i.e.  $\Pi_{\text{sol}} = \Delta p_{\text{sol}}$  and  $\Pi_w = \Delta p_w^{\circ}$  (Fig. 1)."

Thus, there is no contradiction to "the osmotic pressure is measured by the hydrostatic counter-pressure needed to stop the migration flow through the membrane". It is not correct that a hydrostatic counter-pressure is needed to stop the migration flow through the membrane. The "migration flow" stops when the solution is in equilibrium.

- *Lescroart: page 8169 : lines 23 and 24 : in contradiction with the BOF.*

- Reply:

There is no such "BOF" and no contradiction. We state "A change of the pure water (reference) volume that provides information about the water amount that hydrates the solute,  $\Delta V_w^{\circ}$ ."

Again, the volume change is caused by the hydrating water molecules that drive the dissolution/dissociation.

- *Lescroart: page 8169 : line 25 and following : the generalization doesn't hold e.g. because of the geometric constraints.*

- Reply:

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At equilibrium, the geometry of the device does not matter, while the "volume expansion" we consider is due to the amount of water consumed by dissolution/dissociation, independent from water molecules condensing from the gas phase (due to the applicability of the gas-solution analogy), changing an initial volume of water vapor, and when they are supplied by a reservoir such as the right compartment of Fig. 1.

- *Lescroart: page 8170 : lines 14 and 15 : the main compound of  $\Delta V_{\text{sol}}$  is the input flow  $\Delta V_{\text{w}}^{\circ}$  which (see BOF) are not the same as the water "consumed" by hydration and hence not taken into account  $\Delta V_{\text{s,w(hyd)}}^{\pm}$ . This clearly shows that the authors do not understand what happens in the Pfeffer cell.*

- Reply:

On page 8170, 16 and 17 we have summarized the various volume contributions : "The total volume change  $\Delta V = \Delta V_{\text{sol}} + \Delta V_{\text{w}}^{\circ}$  is determined by the volume change of the solution  $\Delta V_{\text{sol}} = \Delta V_{\text{s(dry)}}^{\circ} + \Delta V_{\text{s(diss)}}^{\pm} + \Delta V_{\text{s,w(hyd)}}^{\pm}$  and of pure water  $\Delta V_{\text{w}}^{\circ} = \Delta m_{\text{w}}^{\circ} / \Delta \rho_{\text{w}}^{\circ}$ ."

We have furthermore clearly stated on page 8170, 14 and 15 that: "A change of the volume  $\Delta V_{\text{s,w(hyd)}}^{\pm}$  due the amount of water that is bound to the solute ions, which drives the dissolution and potential dissociation,  $v_{\text{w}}^{\pm} = v_{\text{w}}^{+} + v_{\text{w}}^{-}$ ."

So, "the water 'consumed' by hydration" is taken into account.

This rather shows that our definitions are not understood by the reviewer than that "This clearly shows that the authors do not understand what happens in the Pfeffer cell"!

- *Lescroart: page 8170 : lines 14 and 15 :  $\Delta p_{\text{sol}}$  and  $\Delta p_{\text{w}}^{\circ}$  are defined but not  $p_{\text{sol}}$  and  $p_{\text{w}}^{\circ}$ ;*
- Reply: Correct,  $p_{\text{sol}}$  and  $p_{\text{w}}^{\circ}$  are not defined here; they refer to the equilibrium pressure of the solution and of pure water, respectively, after the addition of the

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solute, as mentioned a few lines later on page 8171, lines 13-14. This will be changed in the revised manuscript.

- *Lescroart: page 8170 : when studying energy balances, the authors should start by defining the system, its limits and the properties of its boundaries;*

- Reply:

We have done this; see Fig. 1, but will further improve this.

- *Lescroart: page 8170 :  $p.V$  has the dimension of energy, but that doesn't mean that  $\Delta(p.V)$  is the energy change of the system;*

- Reply:

We do not refer to the energy change of the system, instead we consider associated changes in energy. On page 8170, lines 18-21 we state:

"Thus, we can consider two associated changes in energy (of the solution and of pure water), i.e. the work done by the two compartments due to the volume changes,  $\Delta V_{\text{sol}}$  and  $\Delta V_{\text{w}}^{\circ}$  against the associated pressure changes  $\Delta P_{\text{sol}}$  and  $\Delta P_{\text{w}}^{\circ}$ , at temperature  $T$ , i.e.  $\Delta E_{\text{sol}}^{\pm} = \Delta(P_{\text{sol}} V_{\text{sol}})$  and  $\Delta E_{\text{w}}^{\circ} = \Delta(P_{\text{w}}^{\circ} V_{\text{w}}^{\circ})$ , for which we postulate:  $\Delta E[\text{J}] = \Delta E_{\text{w}}^{\circ} - \Delta E_{\text{sol}}^{\pm}[\text{J}]$ ."

This will be clarified in the revised manuscript.

- *Lescroart: page 8170 : for a given solution,  $\Delta V_{\text{sol}}$  and  $\Delta V_{\text{w}}^{\circ}$  depend on the geometry of the device (see BOF) and not only on what happens in the compartments, hence whatever "energy formula" depending on  $V_{\text{sol}}$ ,  $V_{\text{w}}^{\circ}$ ,  $\Delta V_{\text{sol}}$  and  $\Delta V_{\text{w}}^{\circ}$  cannot be true in general and equation (2) is irrelevant*

- Reply:

As noted above, the geometry of the device does not matter at equilibrium. Thus, equation (2) is not irrelevant. This will be clarified in the revised manuscript.

- *Lescroart: page 8171, line 9, equations (4) and (5) : - in the present problem, it is not possible to have  $\Delta p$  or  $\Delta V$  as integration limits; furthermore: -  $p$  and  $V$  are not defined but according to lines 13 and 14, are final equilibrium values; - according to (4),  $\Delta p$  and  $\Delta V$  are both positive; -  $V$  being a final value,  $\Delta V < V$  and  $\ln(\Delta V/V) < 0$ ; - hence  $\ln(\Delta p/p) < 0$  and  $\Delta p > p$  : the increase in pressure is larger than the final pressure; - the same demonstration is possible starting with  $\Delta p < p$ , ...*

- Reply:

This is indeed confusing, however, if interpreted correctly not wrong: according to Raoult's law  $\Delta p$  decreases, while the total volume increases, so that  $\ln(\Delta p/p) < 0$  while  $\ln(\Delta V/V) > 0$ . Thus, there is actually nothing wrong with Eq. (4) and (5). But we admit, this is not well defined – it will be clarified in the revised manuscript.

Note that we consider changes, i.e. the two shaded areas in Fig. 1. This we clearly state on page 8171, lines 12-14: "with  $\Delta P[\text{Pa}]$  and  $\Delta V[\text{m}^3]$  the total changes (relative to the initial state) in pressure and volume that correspond to the two shaded areas in Fig. 1 and  $P$  and  $V$  the equilibrium state after the addition of the solute."

- *Lescroart: notes on page 8172, 8173, 8174*

- Reply:

The issues, including the typo in the equality on p8173 line 23, will be clarified in the revised manuscript. There is no real error nor any issue with dimension, if interpreted correctly – our final Eqs. (9-10f) remain unchanged.

- *Lescroart: notes on page 8175*

- Reply:

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Asking for the meaning of  $v_w^\pm$  or  $v_{w,o}$  is a good but probably not easily answered question:

$v_w^\pm$  accounts for the amount of water consumed when a solute dissolves, and depends on the mass fraction solubility of the solute and its effective stoichiometric (dissociation) constant  $v_e^\pm$ . Since, the masses do not change, only the volumes changes, it might be necessary to calculate the actual number of molecules that e.g. form the hydration shell rather from the associated volume change than directly from  $v_w^\pm$ .

But independently,  $v_w^\pm$  can be regarded as an correction factor which complements other correction factors (e.g. osmotic coefficients, van't Hoff factors, activity coefficients).  $v_w^\pm$ , or better the ratio of  $v_w^\pm/v_e^\pm$  can be simply regarded as a correction factor that accounts for solute-solute and solute-solvent ion interactions.

This, as the other issues, will be clarified in the revised manuscript.

- *Lescroart: notes on the Appendix A*
- Reply:

In accord with the reviewer Appendix A is an essential part of the paper. Therefore, we will present it as the main part in the revised manuscript, with the new sections that put the  $v_w$  concept in context to other concepts (including Köhler theory and various water activity representations), and present equations that relate  $v_w$  to  $x$ ,  $\gamma$ ,  $\phi$ ,  $i$ ,  $\kappa$  and to the mass equivalent growth factor  $g_m(RH)$  and deliquescence humidity (RHD) of single and mixed salt solutes, with tables of additional results of  $v_w$  based calculations of  $g_m(RH)$ ,  $\phi(RH)$  and  $\kappa(RH)$  that agree with E-AIM or H-TDMA measurements, as noted above in the general reply.

Also, we have improved the key equation of single solute molality to account for a better  $g_m$  at RH > 95% (below results remain unchanged). This can be easily

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verified with the little example program to calculate the RHD and hygroscopic growth of NaCl from RHD up to conditions close to water vapor saturation.

Since we will further add a mathematical development of a single parameter parameterization that could be used instead of  $v_w$  and can be easily determined from reference data ( e.g. E-AIM  $\phi$  or RHD predictions,  $\kappa$  H-DTMA measurements, etc.), we are confident that all issues raised in the review of Appendix A will be clarified. However, instead of a lengthy point-to-point reply, we rather refer to the revised manuscript.

Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/10/C4137/2010/acpd-10-C4137-2010-supplement.zip>

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 8165, 2010.

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testEQSAM3.j  
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```
1 #! /bin/tcsh -ef
2 pwd
3 set SYSTEM = `uname`
4 if ($SYSTEM == "Darwin") then
5   set f90=ifort
6   set open=open
7 else if ($SYSTEM == "Linux") then
8   set f90=lf95
9   set open=gv
10 else
11   set f90=f95
12   set open=gs
13 endif
14 #
15 cat > ./testEQSAM3.f90 <<EOF
16 PROGRAM testEQSAM3
17 !
18 ! DESCRIPTION
19 ! -----
20 ! Test the EQSAM3 box model and concept w.r.t. NaCl
21 !
22 ! AUTHOR
23 ! -----
24 ! Swen Metzger <swen.metzger@mpic.de>, 16. June 2010
25 !   Department of Atmospheric Chemistry,
26 !   Max Planck Institute for Chemistry, Mainz, Germany.
27 !   Copyright 2010+. All rights reserved.
28 !
29 ! For more details see:
30 !
31 ! (1) http://www.mpch-mainz.mpg.de/~metzger/emac/eqsam3.html
32 ! (2) http://www.atmos-chem-phys.net/7/3163/2007/acp-7-3163-2007.html
33 ! (3) http://www.atmos-chem-phys-discuss.net/10/8165/2010/acpd-10-8165-2010.html
34 !
35 IMPLICIT NONE
36 !
37 INTEGER,PARAMETER :: dp = SELECTED_REAL_KIND(12,307)
38 !
39 INTEGER, PARAMETER :: IO = 1 ! I/O Unit number
40 INTEGER           :: i      ! loop index
41 REAL(dp)          :: sw,RH,RHD,WH20,vw
42 ! check water uptake of NaCl; these values are explained in (2) and (3)
43 REAL(dp),PARAMETER :: ns=1.e-6_dp          ! NaCl "concentration" [mol] - concentration w.r.t. per m3(air)
```

Fig. 1.

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```

44 REAL(dp),PARAMETER :: Ms=58.440_dp          ! molar mass NaCl [g/mol]
45 REAL(dp),PARAMETER :: Mw=18.015_dp          ! molar mass H2O [g/mol]
46 REAL(dp),PARAMETER :: Ws=0.2647_dp         ! mass fraction solubility of NaCl [-]; Ws=ms/(ms+mw); ms=mw/(1/Ws-1)
47 REAL(dp),PARAMETER :: mmw=1000._dp        ! initial mass of H2O [g]
48 REAL(dp),PARAMETER :: mms=mmw/(1._dp/Ws-1._dp) ! maximum mass of NaCl [g] that can be dissolved in 1 kg H2O at saturation
49 REAL(dp),PARAMETER :: nsat=mms/Ms          ! number of moles of NaCl in a saturated solution of 1 kg water [mol]
50 REAL(dp),PARAMETER :: nwat=mmw/Mw         ! inverse mass fraction of 1 mole of H2O in 1 kg water = 55.51[kg/kg]
51 REAL(dp),PARAMETER :: ve=2._dp            ! effective stoichiometric coefficient of solute NaCl [-]
52 REAL(dp),PARAMETER :: RHmax=95._dp        ! maximum RH [%]
53 !
54 OPEN(unit=IO,file='./testEQSAM3.txt', status='unknown',form='formatted')
55 !
56 vw=log10(2._dp/ve*Ms)+2._dp                ! effective stoichiometric coefficient of water [-]; Eq. A2 of (3)
57 RHD=1._dp/(ve/vw*nsat**(ve/vw)/nwat+1._dp) ! deliquescence humidity of NaCl [-]; Eq. A10 of (3)
58 !
59 WRITE(IO,'(6(A,F13.7))') '# - ns', ns, ' - Ms', Ms, ' - mms', mms, ' - nsat', nsat, ' - ve', ve, ' - RHD ', RHD
60 WRITE(IO,'(6(A,F13.7))') '# - Ws', Ws, ' - Mw', Mw, ' - mmw', mmw, ' - nwat', nwat, ' - vw', vw, ' - RHmax', RHmax
61 !
62 DO i=1,int(RHmax)
63   ! fractional relative humidity
64   RH = float(i)/100._dp
65   ! solute activity [kg/kg(H2O)]; Eq. A8 of (3)
66   ! sw = (vw/ve*nwat*(1._dp/RH-1._dp))**(vw/ve)
67   ! update / new interpretation of the solute activity Eq. A8 of (3);
68   ! dimensions now in [kg/kg], since nwat and Ws are both mass fractions;
69   ! the difference yield the remaining free water - required instead of total water
70   ! initial water mass mmw = 1kg
71   ! solute bound water in the solution: mbw=mmw*(1-Ws)
72   ! remaining free water in the solution: mfw=mmw-mbw
73   ! sw = (vw/ve*nwat*(1._dp/RH-1._dp)-2._dp/ve*Ws)**(vw/ve)
74   sw = (vw/ve*nwat*(1._dp/RH-1._dp)-ve/vw*Ws)**(vw/ve)
75   ! aerosol associated water mass [ug(H2O)]; Eq. A9 of (3)
76   IF (RH >= RHD) &
77     WH2O = ns / sw * 1.e9_dp
78   WRITE(IO,'(I3,3F15.6)') i, RH*100, sw, WH2O
79 END DO
80 !
81 CLOSE(IO)
82 !
83 STOP
84 !
85 END PROGRAM testEQSAM3
86 EOF

```

Fig. 2.

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```
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```

```
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```

```
87 #
88 $f90 ./testEQSAM3.f90 -o testEQSAM3.exe
89 ./testEQSAM3.exe
90 cat ./testEQSAM3.txt
91 #
92 cat > ./testEQSAM3.plot << EOF
93 set term postscript color
94 set output 'testEQSAM3_NaCl.ps'
95 set grid
96 set title "1 [umol/m3(air)] NaCl (single solution)"
97 set ylabel "Aerosol Water [ug/m3(air)]"
98 plot "testEQSAM3.txt" using 2:4 ti "EQSAM3", \
99 "E-AIM_NaCl.txt" using 18:19 ti "E-AIM"
100 EOF
101 #
102 gnuplot ./testEQSAM3.plot
103 #gs ./testEQSAM3_NaCl.ps
104 rm testEQSAM3.exe testEQSAM3.f90 testEQSAM3.plot
105 #exit
106 ps2pdf ./testEQSAM3_NaCl.ps
107 rm ./testEQSAM3_NaCl.ps
108 $open ./testEQSAM3_NaCl.pdf
109 #
110 exit
111 #
112 #
113
```

Fig. 3.

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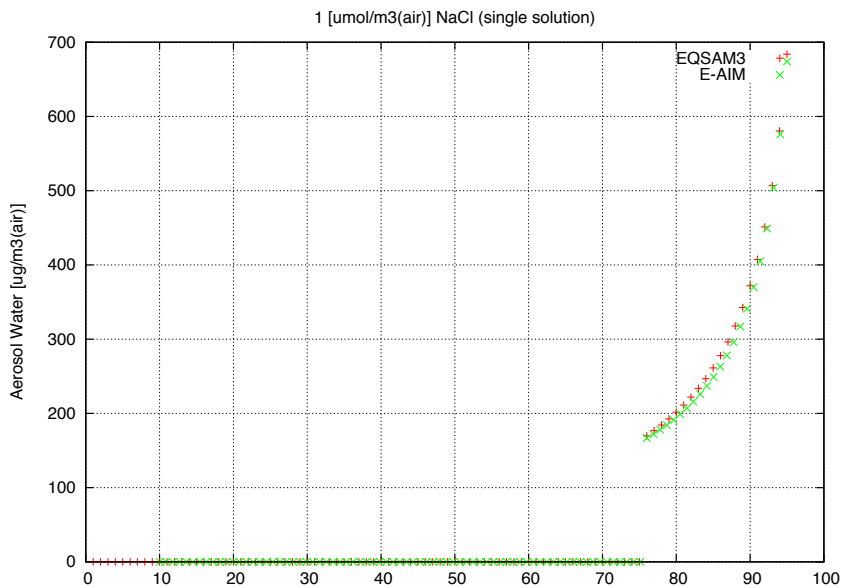
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Fig. 4.

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