

Derivation of the stoichiometric coefficient of water (ν_w) to account for water uptake by atmospheric aerosols

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The authors claim to have derived the effective stoichiometric coefficient of water ν_w from first principles. This is not true. On page 8173, line 23, they introduce artificially, without scientific explanation, an arbitrary scaling factor featuring ν_w . This is how ν_w comes into final play. There is no derivation from whatever scientific principles at all. In my opinion, this procedure alone is enough to reject the paper. But in the same line, a fundamental mathematical error appears. Once corrected, the final expression of ν_w is totally different and yields very different numerical values (see below).

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.

page 8167 :

- lines 16 and 18 : two very different values for the same constant $m_w^0 = 1$ kg and $m_w^0 = 162.33$ g (Metzger et al. 2007 (ML07)).
- lines 17 and 18 : contradiction in values of n_s^{sat} : "1" on line 17, "6.16" on line 18.
- line 19 : n_s^{sat} is not well defined : one should add "in 1 kg of water".
- lines 20 to 23 : it is shown nowhere in the paper that ν_w should have the same value in saturated and non saturated solutions.

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) :

- just adding NaCl to water (not considering osmosis 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;
- hence, the level in the left pipe would rise only slightly due to this process alone;
- 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;

- but the hydration process "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 the migration through the membrane into the solution;
- hence, some net water flow invades the solution coming from the pure water compartment;
- 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;
- hence the amount of water that migrates into the salt solution depends not only on the strength of the hydration pull (depending on the nature of the solute and its concentration) 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.

Some of the comments that follow have to be viewed in the light of these "basic osmosis facts" (BOF).

page 8168 :

- lines 12 and 13 : confusing and ambiguous use of the word "volume", here in moles, below in m^3 , without distinction.
- lines 13 to 16 : as I read it, volume and number of moles are proportional; to make sense, this means that here the volume is in m^3 : so, if (by ionization) the number of moles of particles increases, then the volume (in m^3) should do also, proportionally. In contradiction with BOF.
- 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").

page 8169 :

- lines 6 to 8 : as I read it, the authors consider the volume expansion to be due to the ionization which is not true.
- 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).
- lines 10 to 15 : in contradiction with the BOF.
- line 15 : in contradiction with the initial assumptions (page 8169, lines 1 and 2) : the solution in the left compartment is saturated from the start, before any osmotic migration.

- line 16 : there can be no saturation anymore, because some additional water has migrated into the solution.
- 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 $\Delta p_{sol} - \Delta p_w^0$ with $\Delta p_w^0 < 0$; hence notations Π_{sol} and Π_w are not suitable; I cannot imagine what "the osmotic pressure of pure water" (Π_w) could be.
- lines 23 and 24 : in contradiction with the BOF.
- line 25 and following : the generalization doesn't hold e.g. because of the geometric constraints.

page 8170 :

- lines 14 and 15 : the main compound of ΔV_{sol} is the input flow ΔV_w^0 which (see BOF) is not the same as the water "consumed" by hydration and hence not taken into account in $\Delta V_{s,w}^{\pm(hyd)}$. This is not in agreement with what really happens in the Pfeffer cell (see BOF).
- line 21 :
 - Δp_{sol} and Δp_w^0 are defined but not p_{sol} and p_w^0 ;
 - when studying energy balances, the one should start by defining the system, its limits and the properties of its boundaries, which is not done here;
 - $p.V$ has the dimension of energy, but that doesn't necessarily mean that $\Delta(p.V)$ is the energy change of the system;
 - for a given solution, ΔV_{sol} and ΔV_w^0 depend on the geometry of the device (see BOF) and not only on what happens within the solution, hence whatever "energy formula" depending on V_{sol} , V_w^0 , ΔV_{sol} and ΔV_w^0 cannot be true in general and equation (2) is irrelevant.

page 8171 :

- line 9, equations (4) and (5) :
 - in the present problem, it is not possible to have Δp or ΔV as integration limits;
 - furthermore :
 - * p and V are not defined but according to lines 13 and 14, are final equilibrium values;
 - * according to (4), Δp and ΔV 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 cannot be larger than the final pressure;
- * the same demonstration is possible starting with $\Delta p < p, \dots$

page 8172 :

- lines 3 and 8 : factor 2 should be dropped;
- line 11 :
 - just as p, m is not defined (e.g. line 13);
 - equation (6) is based on equation (5) hence false with the same kind of impossible variations;
- line 6 : $V = A^0 \cdot h$ is false : the section is not constant along the entire height h ;
- line 12 : $\Delta m = m_s$ is not the same as the $\Delta m = \Delta p \cdot A/g$ from equation (6), hence equation (7) doesn't follow from equation (6);
- line 13 : $w_s = m_s/m$: which m ? The initially mass on the left : $m_w^0 + m_s$ (line 5) or $+\Delta m_w^0$?
- lines 12 to 18 :
 - very confusing paragraph;
 - $\Delta m_w^0 = w_s \cdot m_w^0$: false, it would mean that the water flow Δm_w^0 depends only on saturation characteristics although (see BOF) it also depends on the geometry of the device (absent in the formula).
- line 19, equation (7) : meaningless because $w_s < 1$, so $\Delta h > h$ (change is larger than final value) where in addition h is not well defined (see line 6).

page 8173 :

- line 2 : the ideal gas law isn't written like this and Π is ill defined;
- line 8, equation (8) :
 - what is the physical meaning of "the osmotic pressure of pure water" (Π_w^0) ?
 - how does the lhs relate to equation (5) ?
 - van 't Hoff is written, for dilute solutions only, $\Pi = i \cdot M \cdot R \cdot T$ with M the molar concentration (n/V), R the ideal gas constant and T the temperature;
 - van 't Hoff is only valid for the solute, not for the water !

- hence equation (8) is not valid;
- if $\ln(\Delta n_s/\Delta n_w^0) = 0$, then $\Delta n_w^0 = \Delta n_s = \nu_e^\pm \cdot n_s^0$ and
 - * water transfer depends on solute characteristics only (not even saturation), in contradiction with BOF;
 - * but even, salts with the same Δn_s will not necessarily cause the same osmotic pull;
- line 11 : from $\Delta m_w^0 = w_s \cdot m_w^0$, we obtain $\Delta n_w^0 = w_s \cdot n_w^0$ which in our case would yield $\Delta n_w^0 = 2.39$ moles in contradiction with equation (8) where we get $\Delta n_w^0 = 2$ moles.
- lines 13 and 14 : what is the physical meaning of this sentence ?
- line 15 : $w_s = h/\Delta h$ would entail $\Delta h = 3.78h$, with h the final value (see page 8172, line 6).
- line 17 :
 - new definition of h , totally different from page 8172, line 6;
 - what does Δh mean with this new definition ?
- line 21 : factor 2 to be dropped, see comment on page 8172, line 3;
- line 23 :
 - why introduce a scaling factor ?
 - what is its scientific meaning ?
 - if h' is dimensionless, then there is a dimension conflict : $\Delta V_{s,w}^\pm$ is in m^3 and $\Delta A'$ is certainly not;
 - artificial introduction of ν_w^\pm . It is this and only this ν_w^\pm we find in the final equation (10e); this means that ν_w^\pm has not been derived from whatever scientific principle, but instead forced arbitrarily into the development !
 - the last equality is false : x^a/x^b is not equal to $x^{a/b}$! With this error corrected, the same development (which should be better commented) would in the end yield (in stead of equation (10d)) : $\nu_w^\pm = -1 - \frac{3 \ln 10}{\ln(w_s \cdot \frac{2}{\nu_e^\pm})}$
 - with, in our special case, 4.197 as the final value instead of 1.423;
 - this also means that the authors were not able to introduce a suitable scaling factor.
- line 24 : according to the formula, the more bound water molecules, the smaller the corresponding height, which seems counterintuitive;

- line 19 until page 8174, line 8 : the authors should better develop this part so the reader could follow their physical reasoning.

page 8174 :

- line 1 : nothing involves the use of Archimedes' principle;
- line 4 : an "effective change in density" cannot be dimensionless ?
- line 5 : what is the scientific meaning of a "unit change in the pure water density" ?
- line 7 : how can a "ratio of density expressions" have a dimension ?
- line 12 : $\ln \varrho_w^0$ with ϱ_w^0 [kg/m^3] ?
- line 13 : what is the scientific meaning of the "the fractional density of pure water" ?

page 8175 :

- line 1 : should be more explicit;
- line 10 : how does, as stated here, $\nu_{w,0} = -1$ indicate that each mole of solute consumes $\log_{10}(2 \times 1000 \cdot w_s / \nu_e)$ moles of initially free water ? And what is the meaning of $\nu_{w,0}$?
- line 16 : NaCl : $\nu_w^\pm = 1.423$
 - according to the definition, this is the number of moles hydration water of 1 mole NaCl; in contradiction with the value of the formula in line 11 : 2.423 moles;
 - hydration needs much more water (see review of Appendix A), this is not even an acceptable approximation ! It is general knowledge (e.g. "Molecular Driving Forces" by K. A Dill and S. Bromberg, 2003) that the Na^+ and Cl^- ions are surrounded by shells of numerous water molecules : 4 to 6 molecules in the first shell, 10 or so in the second one.

I have already reviewed the Appendix A (page 8178 and following) in another document : Review of the revised paper of Xu et al. For the sake of completeness it is added below.

As a conclusion, one has to admit that there is no such thing as a physically sound derivation of the stoichiometric coefficient of water ν_w from first principles. Therefore the paper should be rejected.

But also, publishing the revised version of Xu et al. would implicitly give the developments in Metzger et al. 2007 and Metzger et al. 2010, a scientific existence they do not deserve according to my understanding.

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26/04/2010

Review of the Appendix A

Due to the specificity of my expertise, my review will concentrate on the appendix only i.e. “Clarification of the EQSAM3 concept (Metzger and Lelieveld, 2007)”.

Scientifically speaking, this appendix is nevertheless an essential part of the paper because :

- it was requested by the editor as a condition of submission of the revised paper,
- its role is to display, in a clear and understandable way, the scientific basis of the EQSAM3 model.

Therefore it is necessary to examine how the equations are obtained and what physical meaning they carry.

First of all, as a general remark, too many symbols are not defined. Hence, some formulas and equations are difficult or even impossible to understand.

Equation (A-1)

This is equation (19) in Metzger et al. 2007 (ML07).

- This pivot equation which shows how ν_w allegedly depends on the solubility and therefore is at the core of the EQSAM3 “model”, is still not explained nor derived properly here. Hence, my comments published during the review of Xu et al. 2009 (XPML09) are still valid because they’ve not been addressed seriously.
- The Final reply by Xu et al. on 24. December 2009 contains an 8-page “Derivation of ν_w ” by S. Metzger. It is evident to me that this text creates even more problems and generates more errors than ML07 itself. As an instance, the author erroneously tries to link the osmotic pressure with the amount of hydration water, not taking into account the geometric details by which the hydrostatic counter-pressure in the Pfeffer cell builds up.

Therefore I feel that the derivation of ν_w should be peer-reviewed and accepted for publication in a respected journal before the Xu et al. 2010 manuscript itself could be accepted.

To stay with the present appendix however, here are some complementary comments :

- Translated into numerics for NaCl with $\nu_e = 2$, $w_s = 0.2647$ and $\nu_w = 1.422$ (table 1a, ML07), lines 4 and 5 (page 27) yield : each mole of NaCl consumes 2.422 moles of water. This is an unrealistic figure because it is general knowledge (e.g. “Molecular Driving Forces” by K. A Dill and S. Bromberg, 2003) that the Na+ and Cl- ions are surrounded by shells of numerous water molecules : 4 to 6 molecules in the first shell, 10 or so in the second one.
- In lines 5 and 6, the issue of the unphysical presence of the decimal logarithm has been "fixed" by using the natural logarithm at the cost of introducing the necessary "ln 10" out of nothing (A-2).

Equations (A3a and A3b)

In the calculation of a mole fraction, be it a generalized one, $\nu_w.n_w$ is a quantity without any physical meaning because $\nu_w > 1$ (1.422 for NaCl (table 1a, ML07)) and hence $\nu_w.n_w$ is designating more moles of water than really available. It cannot refer to some ionization multiplication effect because hydration doesn't ionize the water molecules.

Hence \tilde{x}_s and \tilde{x}_w have no physical meaning either and it is meaningless to build any physical reasoning on them.

Equation (A4a)

a_w (water activity) and RH (relative humidity) have a definite physical meaning. Hence they cannot be equated to the meaningless \tilde{x}_w . Therefore, most of the equations that follow are insubstantial, especially from (A-2.2b) to (A-2.6), plus (A-3), (A-4.1), (A-4.2) and (A-5).

Page 8181, lines 18 and 19

Where does the exponent ν_e/ν_w come from ?

Sloppy writing of fractions

Equation (A8)

Dimensional conflict : mass lacking.

Equation (R1) 2nd line

These equations are supposed to summarize the solvation and hydration process, by taking explicitly into account the hydration water :

- If, as suggested by the equation, ν_e^\pm moles of NaCl ionize into ν_e^+ moles of Na+ ions and ν_e^- moles of Cl- ions, then $\nu_e^\pm = \nu_e^+ = \nu_e^-$ (= 1 if

complete dissociation, as is the case here). But on line 6, page 29 we read $\nu_e^\pm = \nu_e^+ + \nu_e^-$ and according to table 1a, ML07, $\nu_e = 2$ for NaCl.

- $\nu_e^\pm > 1$, $\nu_e^+ \leq 1$ and $\nu_e^- \leq 1$ can be interpreted as molar fractions (number of ions compared to number of initial molecules), but $\nu_w^\pm > 1$ cannot, because there is almost no ionization of the water involved here.
- Dissociation of NaCl needs hydration water. According to (R-1) :
 - every Na⁺ ion will be surrounded by ν_w^+/ν_e^+ H₂O molecules, in the present case ν_w^+ H₂O molecules
 - every Cl⁻ ion will be surrounded by ν_w^-/ν_e^- H₂O molecules, in the present case ν_w^- H₂O molecules;
 - hence, every dissociated NaCl molecule "consumes" $\nu_w^\pm = \nu_w^+ + \nu_w^- = 1.423$ (table 1a, ML07), in contradiction with the number 2.422 of line 4, page 27 (see comments on Equation (A-1)); this result would also mean that because $\nu_w^\pm \leq 2$, some ions are simply not hydrated.
- And, once again, it is widely accepted that the hydration of an NaCl molecule involves much more water molecules : between 10 and 20, organized in superposing shells.

In my opinion, the Appendix doesn't meet the objective of giving the necessary confidence in what is presented as the underlying thermodynamic principles of the EQSAM3 "model". And then, basing further work and comparisons with this "model" on the unique finding that it has results similar to those from EQUISOLV II, perhaps for bad reasons, would be risky, misleading and unscientific. Therefore I have to recommend that the paper should not be accepted, at least until a peer-reviewed derivation of the basic equations underlying that model is published.

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24/03/2010