

This discussion paper is/has been under review for the journal Atmospheric Chemistry and Physics (ACP). Please refer to the corresponding final paper in ACP if available.

**Derivation of the  
stoichiometric  
coefficient of water**

S. Metzger et al.

# Derivation of the stoichiometric coefficient of water ( $\nu_w$ ) to account for water uptake by atmospheric aerosols

S. Metzger<sup>1</sup>, B. Steil<sup>1</sup>, J. E. Penner<sup>3</sup>, L. Xu<sup>3</sup>, and J. Lelieveld<sup>1,2</sup>

<sup>1</sup>Max Planck Institute for Chemistry, Mainz, Germany

<sup>2</sup>Energy, Environment and Water Research Centre, The Cyprus Institute, Nicosia, Cyprus

<sup>3</sup>Department of Atmospheric, Oceanic and Space Science, University of Michigan, Ann Arbor, Michigan, USA

Received: 19 March 2010 – Accepted: 22 March 2010 – Published: 29 March 2010

Correspondence to: S. Metzger (swen.metzger@mpic.de)

Published by Copernicus Publications on behalf of the European Geosciences Union.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## Abstract

In this work we derive the effective stoichiometric coefficient of water ( $v_w$ ), introduced by Metzger and Lelieveld, 2007 (ML07), from first principles. We give examples of the application of  $v_w$  in CPU efficient computations of the Deliquescence Relative Humidity (DRH) and the water uptake of atmospheric aerosols, being important parameters in atmospheric chemistry and climate modeling. We show that the application of  $v_w$  in a gas/liquid/solid aerosol equilibrium partitioning model (EQSAM3) leads to results that are in excellent agreement with those of widely used thermodynamic (reference) models (E-AIM and ISORROPIA2) for various single salt solutions (NaCl,  $\text{NH}_4\text{NO}_3$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NH}_4\text{HSO}_4$ ,  $\text{NaHSO}_4$ ) and the corresponding mixed solutions (including  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$  and  $\text{Na}_3\text{H}(\text{SO}_4)_2$ ), notwithstanding the distinct different theoretical and numerical concepts on which these models are based.

## 1 Introduction

Metzger and Lelieveld, 2007 (ML07) introduced the effective stoichiometric coefficient of water  $v_w$  in analogy to the stoichiometric coefficient of solutes to consistently account for the amount of water that is consumed during the hydration of solutes. This complements the traditional physical chemistry methods, considering that the amount of water is not normally considered in detail in the classical equilibrium thermodynamics based on chemical potentials and inferred activity coefficients. The use of  $v_w$  can have the important advantage of decreasing CPU requirements by efficiently computing comprehensive aerosol equilibrium thermodynamics in large-scale models of the atmospheric environment. However, the scientific concept was questioned in the public discussion of the application paper of Xu et al. (2009). To underscore that the new concept of  $v_w$  is scientifically sound and useful, we derive the effective stoichiometric coefficient of water ( $v_w$ ) from first principles. Moreover, we present results from a comparison of our Equilibrium Simplified Aerosol Model 3, EQSAM3 (ML07), applying  $v_w$ , with the

## Derivation of the stoichiometric coefficient of water

S. Metzger et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



reference thermodynamic models E-AIM (Wexler and Clegg, 2002) and ISORROPIA2 (Fountoukis and Nenes, 2007), the latter used in atmospheric chemistry-transport models.

In Sect. 2 we derive  $v_w$  and apply it in Sect. 3, in which we also provide example calculations and present a model inter-comparison. We conclude in Sect. 4 with a brief summary and the context of the underlying concepts, while the key equations on which EQSAM3 is built and that are relevant for our applications are summarized in the appendix.

## 2 Derivation of $v_w$

Let us consider the following experiment, adding a solute to pure water. When the solution becomes saturated any excess of the solute will not dissolve and precipitate from the solution. The critical mass of the solute  $m_{s(\text{solid})}$  [kg] that yields a saturated solution is related to the water mass  $m_w^0$  [kg], by the mass fraction solubility, which is defined as  $w_s[-] = m_{s(\text{solid})}$  [kg] / ( $m_{s(\text{solid})}$  [kg] +  $m_w^0$  [kg]). Considering for instance sodium chloride ( $\text{NaCl}_{(\text{cr})}$ ), where  $w_{s(\text{NaCl})} = 26.47$  [%] (at  $T = 25$  °C), a (dry=solid=crystalline) maximum mass of  $m_{s(\text{solid})} = 0.36$  [kg] can completely dissolve in a mass  $m_w^0 = 1$  [kg] of pure water. Alternatively, if we consider 1 mole of  $\text{NaCl}_{(\text{cr})}$ , a mass of  $m_{s(\text{solid})} = n_s^{\text{sat}} M_s = 58.44$  [g] can dissolve in a mass  $m_w^0 = 1000$  [g] /  $n_s^{\text{sat}} = 162.33$  [g] of pure water. With these mass ratios the solution is saturated.  $n_s^{\text{sat}}$  denotes the number of moles of solute at saturation and corresponds to the solubility mass fraction  $w_s[-]$ , which is the central parameter. Note that we consider here the special case of a saturated solution in order to be able to derive  $v_w$ . However, once  $v_w$  is known, its use is not restricted to a saturated solution as it will be shown below.

The number of “free” water molecules decreases during dissolution, while the total water mass does not change, since some of the water molecules are “consumed” by

### Derivation of the stoichiometric coefficient of water

S. Metzger et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

the solute, either bound to the solute as a hydration shell, or by processes such as hydrolysis.

To describe this amount of “consumed” (bound) water (i.e. solvent) molecules, expressed as an equivalent of chemical stoichiometry, i.e. as a molar change, Metzger and Lelieveld (2007) (ML07) have introduced the symbol  $v_w$ , the “stoichiometric” coefficient of water. Note that  $v_w$  is analogous to the stoichiometric coefficient of the solute  $v_s$ , used in chemistry to express in how many moles an ion-pair can dissociate. For instance, strong electrolytes such as  $\text{NaCl}_{(\text{cr})}$  dissociate practically completely in water so that 1 mole of  $\text{NaCl}_{(\text{cr})}$  yields 1 mole of  $\text{Na}^+_{(\text{aq})}$  and 1 mole of  $\text{Cl}^-_{(\text{aq})}$ , thus 1 mole of dry (crystalline) solute yields  $v_s=2$  moles ions of electrolyte in solution.

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. 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  $v_w$ .

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. We can derive the stoichiometric coefficient of water  $v_w^\pm$  by considering for our experiment an osmosis system according to ML07. In a Pfeffer cell (Pfeffer, 1887), with two compartments expandable in height (with equal surfaces), the volumes can expand by exerting different pressures. The pressure difference is merely the result of solute dissolution and potential dissociation that causes the volume expansion and the consequent hydrostatic counter-pressure. A schematic is given in Fig. 1.

## Derivation of the stoichiometric coefficient of water

S. Metzger et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## Derivation of the stoichiometric coefficient of water

S. Metzger et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Assume that both compartments are filled with a certain mass of pure water that corresponds to the saturation of 1 mole of solute (e.g. of  $\text{NaCl}_{(\text{cr})}$  with the values given above), and that these volumes are separated through a membrane permeable only for water molecules but not for the solute molecules, independently whether these are dissociated (hydrated) or not. 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  $\nu_{\text{e}}^{\pm}$  moles in which the solute effectively dissociates and due to  $\nu_{\text{w}}^{\pm}$ , the amount of water consumed during dissolution/dissociation.

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.

At saturation the system is in equilibrium again with maximum changes in the volume of both compartments,  $\Delta V_{\text{sol}}$  and  $\Delta V_{\text{w}}^{\circ}$ , 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  $\Delta p_{\text{w}}^{\circ}$ , that build up due to the volume expansion compensate the osmotic pressures, i.e.  $\Pi_{\text{sol}} = \Delta p_{\text{sol}}$  and  $\Pi_{\text{w}} = \Delta p_{\text{w}}^{\circ}$  (Fig. 1).

Thus, we distinguish between two volume changes:

1. A change of the pure water (reference) volume that provides information about the water amount that hydrates the solute,  $\Delta V_{\text{w}}^{\circ}$ . Note that this is valid, both, when the water molecules condense from the gas phase (shown below based on the classical gas-solution analogy), thus changing an initial volume of water vapor, and when they are supplied by a reservoir such as the right compartment of Fig. 1.

## Derivation of the stoichiometric coefficient of water

S. Metzger et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

2. A change in the volume of the solution due to the additional solute and hydration,  $\Delta V_{\text{sol}}$ .

Note that the volume change for (1) needs to be considered for pure water only, while the volume change (2) consists of three parts:

- 5 1. A change of the volume due to the added mass of solute,  $\Delta V_{\text{s(dry)}}^{\circ}$ ; this volume corresponds to the initial mass of the solute that does not change by the dissolution of a solute, e.g. due to solute hydration (which is not a chemical reaction);
2. A change of the volume  $\Delta V_{\text{s(diss)}}^{\pm}$  due to solute dissociation, expressed by the effective stoichiometric coefficient of the solute,  $v_{\text{e}}^{\pm} = v_{\text{e}}^{+} + v_{\text{e}}^{-}$ ; (one mole of a single charged electrolyte (ion-pair) such as NaCl yields one mole,  $v_{\text{e}}^{+} = 1$ , of the of the cation ( $\text{Na}_{(\text{aq})}^{+}$ ) and one mole,  $v_{\text{e}}^{-} = 1$ , of the anion ( $\text{Cl}_{(\text{aq})}^{-}$ ). Thus, for NaCl at equilibrium, one mole of dry substance expands in volume into two moles in solution,  $v_{\text{e}}^{\pm} = 2$ ).
- 10 3. 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,  $v_{\text{w}}^{\pm} = v_{\text{w}}^{+} + v_{\text{w}}^{-}$ .
- 15

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  $\Delta V_{\text{w}}^{\circ} = \Delta m_{\text{w}}^{\circ} / \Delta \rho_{\text{w}}^{\circ}$ .

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:

20

$$\Delta E[\text{J}] = \Delta E_{\text{w}}^{\circ} - \Delta E_{\text{sol}}^{\pm}[\text{J}]. \quad (1)$$

Let  $\Delta E = \Delta(PV)$  denote the total change in energy (with potential changes in the heat content), i.e. the work by both compartments due to the effective dissociation of the

solute into  $v_e^\pm$  moles (considering one mole solute) and the changes in the pure water compartment due to  $v_w^\pm$  consumed moles of water.

At equilibrium  $\Delta E=0$ , so that Eq. (1), expressed in terms of partial volume and pressure changes,  $dE=d(PV)=0$ , yields with the product integration,  $d(PV)=dPV+dVP$ :

$$5 \quad dPV[\text{J}] + dVP[\text{J}] = 0. \quad (2)$$

Dividing Eq. (2) by  $P[\text{N/m}^2]$  and  $V[\text{m}^3]$  further yields (with  $[\text{J}=\text{Nm}]=[\text{Pa}=\text{N/m}^2]$ ):

$$\frac{dP[\text{N/m}^2]}{P[\text{N/m}^2]} + \frac{dV[\text{m}^3]}{V[\text{m}^3]} = 0. \quad (3)$$

Integration over all partial changes in pressure and volume yields:

$$\int_P^{(\Delta P)} \frac{dP}{P} + \int_V^{(\Delta V)} \frac{dV}{V} = \ln\left(\frac{\Delta P}{P}\right) + \ln\left(\frac{\Delta V}{V}\right) = 0, \quad (4)$$

10 Equation (4) can be re-arranged into:

$$\ln\left(\frac{\Delta P}{P} \cdot \frac{\Delta V}{V}\right) = 0, \quad (5)$$

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.

15 These changes can be expressed in terms of the total mass change of the solution,  $\Delta m[\text{kg}]$ , caused by the addition of the solute mass  $m_{\text{s(solid)}}[\text{kg}]$  to the left compartment, i.e.  $\Delta m[\text{kg}]=m_{\text{s(solid)}}[\text{kg}]$ . Adding  $m_{\text{s(solid)}}[\text{kg}]$  causes a redistribution of the initial pure water mass  $\Delta m_w^0[\text{kg}]$  from the right compartment; the water mass is conserved. Further, the gravitational acceleration  $g[\text{m/s}^2]$  acts on both mass changes (of the solution and of the pure water).

20

**Derivation of the stoichiometric coefficient of water**

S. Metzger et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## Derivation of the stoichiometric coefficient of water

S. Metzger et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

We can therefore express the total pressure change  $\Delta P$  [Pa] in terms of a change in the resulting total gravitational force  $\Delta F_g$  [N] =  $\Delta m$  [kg] ·  $g$  [m/s<sup>2</sup>] that acts on both surface areas,  $2A$  [m<sup>2</sup>], i.e.  $\Delta P$  [Pa] =  $\Delta F_g$  [N] / ( $2A$  [m<sup>2</sup>]). Analogously, we can express the resulting (total) pressure and volume of the solution at equilibrium in terms of the total mass of the solution,  $m$  [kg] =  $m_w^0$  [kg] +  $m_{s(\text{solid})}$  [kg] as  $P$  [Pa] =  $m$  [kg] ·  $g$  [m/s<sup>2</sup>] /  $A^0$  [m<sup>2</sup>] and  $V$  [m<sup>3</sup>] =  $A^0$  [m<sup>2</sup>] ·  $h$  [m]; with  $A^0$  [m<sup>2</sup>] the total surface area, and  $h$  [m] an associated height of the solution that corresponds to both compartments. If we express the total volume change as a change in height of both compartments  $\Delta V$  [m<sup>3</sup>] =  $2A$  [m<sup>2</sup>] ·  $\Delta h$  [m], with  $\Delta h$  [m] =  $\Delta h_{\text{sol}}$  [m] +  $\Delta h_w^0$  [m], we can express Eq. (5) in terms of a dimensionless ratio of potential energies, i.e. the change relative to the potential energy of the solution:

$$\ln \left( \frac{\Delta m \cdot g}{2A} \cdot \frac{A^0}{m \cdot g} \cdot \frac{\Delta V}{V} \right) = \ln \left( \frac{\Delta m}{m} \cdot \frac{A^0}{2A} \cdot \frac{2A \cdot \Delta h}{A^0 \cdot h} \right) = \ln \left( \frac{\Delta m}{m} \cdot \frac{\Delta h}{h} \right) = 0. \quad (6)$$

The total mass change  $\Delta m = m_s$  of the system is related through the definition of solubility,  $w_s = m_s / m$ , to the associated change in the water mass,  $\Delta m_w^0 = w_s \cdot m_w^0$ , by  $\Delta m = \Delta m_w^0 \cdot m_w^0 / m_w$ , with  $m_w = m_w^0 - \Delta m_w^0$  the remaining free water in the solution and the pure water compartment. The total mass of the system,  $m = m_w^0 + \Delta m$ , can be additionally expressed as  $m = m_w^0 \cdot m_w^0 / m_w$ , so that the mass ratio of the total mass change to the total mass of the system can be expressed as  $\Delta m / m = \Delta m_w^0 / m_w^0 = w_s$ , and Eq. (6) yields:

$$\ln \left( w_s \cdot \frac{\Delta h}{h} \right) = 0. \quad (7)$$

Since Eq. (7) depends on fractions rather than on the actual amounts of solute and water (due to  $w_s$ ), we can consider molar changes to further express the change in height,  $\Delta h$ , relative to the height  $h$  that corresponds to the solution. Although both are not (yet) known, they depend (for molar changes) on the effective stoichiometric coefficients of the solute  $v_e^\pm$  and water  $v_w^\pm$ .



## Derivation of the stoichiometric coefficient of water

S. Metzger et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



This becomes clearer by expressing the energy ratio of Eq. (5) in the terms of the ideal gas law, i.e.  $\Pi \cdot V = \Delta n \cdot R \cdot T$ , based on the gas-solution analogy according to van't Hoff (1887, 1897, 1901) and Einstein (1905). Note that this analogy was resolved after the historical dispute between van't Hoff and Rayleigh versus Kelvin and Gibbs, <http://urila.tripod.com/evidence.htm>).

Thus, if we consider the ratio of the two energy changes expressed in terms of the gas law:

$$\ln \left( \frac{\Pi_{\text{sol}}}{\Pi_{\text{w}}^{\circ}} \right) = \ln \left( \frac{\Delta c_{\text{s}} \cdot R \cdot T}{\Delta c_{\text{w}}^{\circ} \cdot R \cdot T} \right) = \ln \left( \frac{\Delta n_{\text{s}} \cdot R \cdot T / V}{\Delta n_{\text{w}}^{\circ} \cdot R \cdot T / V} \right) = \ln \left( \frac{\Delta n_{\text{s}}}{\Delta n_{\text{w}}^{\circ}} \right) = 0, \quad (8)$$

where  $\Delta n_{\text{s}} = v_{\text{e}}^{\pm} \cdot n_{\text{s}}^{\circ}$  with  $n_{\text{s}}^{\circ} = 1$  [mol] of (dry) solute that has been added to a corresponding mass of pure water to satisfy  $w_{\text{s}}[-]$  as described above, which yields an associated change of the pure water mass  $\Delta m_{\text{w}}^{\circ} = \Delta n_{\text{w}}^{\circ} M_{\text{w}} = w_{\text{s}} \cdot m_{\text{w}}^{\circ}$ ;  $\Delta c_{\text{s}} = \Delta n_{\text{s}} / V$  and  $\Delta c_{\text{w}}^{\circ} = \Delta n_{\text{w}}^{\circ} / V$  are concentration changes, with  $V$  being the total volume of the system, so that the term  $RT/V$  cancels out. Note that these “energy changes” might be expressed instead as the osmotic pressures for each component, since  $P$  is not an energy.

On the other hand, Eqs. (7) and (8) are only satisfied if  $w_{\text{s}} = \frac{h}{\Delta h}$  and  $\Delta n_{\text{s}} = \Delta n_{\text{w}}^{\circ}$ , since then the natural logarithm becomes zero, i.e.  $\ln(1) = 0$ , as required by Eqs. (7) and (8).

The height  $h$  of the solution is an average height of  $\Delta h_{\text{sol}}[\text{m}]$  and  $\Delta h_{\text{w}}^{\circ}[\text{m}]$  and proportional to both,  $v_{\text{e}}^{\pm}$  and to half of the total change  $\Delta h[\text{m}]$ , if divided by a certain scaling factor, i.e.  $h = v_{\text{e}}^{\pm} \cdot \Delta h / (2h')$ , so that the height ratio  $\frac{\Delta h}{h}$  of Eq. (7) can be expressed as  $\frac{\Delta h}{h} = \frac{2}{v_{\text{e}}^{\pm}} \cdot h'$ , where the factor of 2 comes from the fact that  $v_{\text{e}}^{\pm}$  caused a total volume change of  $2A\Delta h$ .

Let us assume that this dimensionless scaling height  $h'$  has a density, volume and surface contribution, i.e.  $\frac{\Delta V_{\text{s,w(hyd)}^{\pm}}}{\Delta A'} = \frac{h' \cdot h' \cdot h'}{h' \cdot h'} \cdot \frac{1}{h'^{-v_{\text{w}}^{\pm}}} = \frac{h'^3}{h'^{2-v_{\text{w}}^{\pm}}} = h'^{3/(2-v_{\text{w}}^{\pm})}$ , which can be attributed to the binding of water molecules, with  $h'^{-v_{\text{w}}^{\pm}}$  an associated height of the bound water molecules. However, a density contribution remains as the final result of the mass and

volume changes of Eq. (5), in accordance with Archimedes' principle, so that a mass ratio in hydrostatics can be expressed in terms of a density ratio (<http://en.wikipedia.org/wiki/Buoyancy>).

Therefore, we assume the dimensionless scaling height  $h'$  being an effective change in density  $\frac{\Delta h}{h} = \frac{2}{v_e^\pm} \cdot h' = \frac{2}{v_e^\pm} \cdot \frac{\rho_w^{o(2-v_w^\pm)/3}}{\Delta \rho_w^o}$ , relative to a unit change in the pure water density; expressed in SI-units,  $\Delta \rho_w^o = 1 \text{ [kg/m}^3\text{]}$ , where we interpret  $\frac{2}{v_e^\pm} \cdot \frac{\rho_w^{o(2-v_w^\pm)/3}}{\Delta \rho_w^o} = \frac{m_w^o}{\Delta m_w^o} = 1/w_s$  as the reciprocal and dimensionless (although the ratio of density expressions might not be dimensionless) mass change to satisfy Eq. (7).

Equation (7) thus yields:

$$\ln \left( w_s \cdot \frac{2}{v_e^\pm} \cdot \rho_w^{o(2-v_w^\pm)/3} \right) = 0. \quad (9)$$

And Eq. (9) can be rearranged into

$$\ln \left( \frac{2}{v_e^\pm} w_s \right) + (2 - v_w^\pm)/3 \cdot \ln(\rho_w^o) = 0. \quad (10a)$$

With the fractional density of pure water in SI-units,  $\rho_w^o = 1000 \text{ [kg/m}^3\text{]}$  at  $T_o = 277.15 \text{ [K]}$ , we can express the dimensionless density ratio as  $\ln(\rho_w^o) = \ln(1000) = 3\ln(10)$ , so that we can write:

$$\ln \left( \frac{2}{v_e^\pm} w_s \right) + (2 - v_w^\pm) \cdot \ln(10) = 0, \quad (10b)$$

and upon re-arranging, we can finally solve for  $v_w^\pm$

$$v_w^\pm = \ln \left( \frac{2}{v_e^\pm} w_s \right) / \ln(10) + 2. \quad (10c)$$

**Derivation of the stoichiometric coefficient of water**

S. Metzger et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



In accordance with the gas-solution analogy the value  $R \cdot T_o = 2.304 \text{ [KJ]}$  is close to  $\ln(10) = 2.303$  assuming a temperature for which pure water has a density of unity,  $\rho_{w(\text{pure})}^o = 1000 \text{ [kg/m}^3\text{]}$ , i.e.  $T_o = 277.15 \text{ [K]}$ , so that we can alternatively write:

$$v_w^\pm = \ln \left( \frac{2}{v_e^\pm} w_s \right) / 2.304 + 2. \quad (10d)$$

5 Furthermore, the ratio of  $\ln \left( \frac{2}{v_e^\pm} w_s \right) / \ln(10)$  can be further reduced to the decadal logarithm, i.e.  $\log_{10} \left( \frac{2}{v_e^\pm} w_s \right)$ , so that Eq. (10c) can be alternatively expressed as

$$v_w^\pm = \log_{10} \left( \frac{2}{v_e^\pm} \cdot w_s \right) + 2. \quad (10e)$$

Finally, by dropping the  $\pm$ -index which indicates the  $\pm$ -ion-pair, we may write:

$$v_w = v_{w,o} + \log_{10} \left( \frac{2}{v_e} \cdot 1000 \cdot w_s \right), \quad (10f)$$

10 with Eq. (10f) being Eq. (19) of ML07, and their  $v_{w,o} = -1$  indicating that each mole of solute “consumes”  $\log_{10} \left( \frac{2}{v_e} \cdot 1000 \cdot w_s \right)$  moles of initially “free” water.

### 3 Application of $v_w$

#### 3.1 Calculations of $v_w$

15 With the above equations we can, for example, calculate  $v_w$  for the following compounds:

$$(A) \text{ NaCl, } w_s = 0.2647, v_e^\pm = 2, v_w^\pm = \frac{1}{2.303} \ln \left( \frac{2}{2} \cdot 0.2647 \right) + 2 = 1.423.$$

## Derivation of the stoichiometric coefficient of water

S. Metzger et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



(B)  $\text{NH}_4\text{NO}_3$ ,  $w_s = 0.6805$ ,  $v_e^\pm = 1.97$ ,  $v_w^\pm = \frac{1}{2.303} \ln \left( \frac{2}{1.97} 0.6805 \right) + 2 = 1.839$ .

(C)  $(\text{NH}_4)_2\text{SO}_4$ ,  $w_s = 0.4331$ ,  $v_e^\pm = 2.15$ ,  $v_w^\pm = \frac{1}{2.303} \ln \left( \frac{2}{2.15} 0.4331 \right) + 2 = 1.605$ .

Thus, these values (among other examples) based on Eq. (10c) are in agreement with those presented in Table 1a of ML07, based on Eq. (10f) i.e. their Eq. (19).

### 3.2 Comparison EQSAM3 with reference models

In this section we present several examples for the application of  $v_w$  with respect to the DRH and the water uptake of atmospheric aerosols, being key parameters in atmospheric chemistry and climate modeling studies. Figure 2 presents the results of a model inter-comparison using the gas/liquid/solid aerosol equilibrium partitioning model EQSAM3 and the widely used and generally accepted thermodynamic models, E-AIM (Wexler and Clegg, 2002; <http://www.aim.env.uea.ac.uk/aim/aim.php>) and ISORROPIA2 (Fountoukis and Nenes, 2007).

Figure 2a–f show the results for various single salt solutions, i.e. NaCl,  $\text{NH}_4\text{NO}_3$ ,  $\text{NH}_4\text{NO}_3$ [nmol],  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NH}_4\text{HSO}_4$ ,  $\text{NaHSO}_4$ , and Fig. 2g–h shows the results for the corresponding mixed solutions (including  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$  and  $\text{Na}_3\text{H}(\text{SO}_4)_2$ ).

All solute concentrations were fixed to  $1[\mu\text{mol}/\text{m}^3]$  except for Fig. 2d, where the solute concentrations were fixed to  $1[\text{nmol}/\text{m}^3]$  to test the sensitivity against a different concentration. The aerosol water and the DRH predicted by EQSAM3 compare well with the predictions of E-AIM and ISORROPIA2 for all salt solutions. The only exception is the  $1[\text{nmol}/\text{m}^3]$  case where ISORROPIA2 does not predict any  $\text{NH}_4\text{NO}_3$ . This is probably related to the equilibrium constant ( $K_{\text{eq}(\text{NH}_4\text{NO}_3)}$ ) used for the  $\text{NH}_4\text{NO}_3(\text{s}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{HNO}_3(\text{g})$  equilibrium reaction, which prohibits the  $\text{NH}_4\text{NO}_3$  formation due to its low value of  $57.46[\text{ppb}^2]$  in ISORROPIA2 (Fountoukis and Nenes, 2007). Note that the EQSAM3 version introduced in ML07 has been extended in this work by an option to account for  $K_{\text{eq}(\text{NH}_4\text{NO}_3)}$  (exactly as used in ISORROPIA2); using

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



the temperature dependent  $K_{\text{eq}(\text{NH}_4\text{NO}_3)}$  yields the same result (not shown) as ISOR-ROPIA2, but differs from that of E-AIM. Note further that the DRH for the mixed solution is inferred from the same equations used to derive the DRH of single solutes (i.e. Eq. 21 and Sects. 4.1.5 and 4.1.9 of ML07; see also the summary of the EQSAM3 key equations given in the appendix) by using the mean values of the required thermodynamic parameters, i.e. the effective stoichiometric coefficients of the solutes and water of all single solutes in the mixed solution, their solubilities and molar masses. Although a few discrepancies occur at the phase transitions, the aerosol water uptake, which is central for our modeling purposes, is generally represented very accurately.

## 4 Discussion and conclusions

In this work we have detailed the concept of the effective stoichiometric coefficient of water ( $\nu_w$ ), as introduced by ML07 to consistently account for the amount of water that is consumed during the hydration of solutes, in analogy to the stoichiometric coefficient of solutes. This concept has been questioned in the public discussion of an application paper by Xu et al. (2009), and we hope to have shown that this was unfounded. The application potential has been corroborated by direct comparisons with the reference model E-AIM of Wexler and Clegg (2002). Our results indicate that our new method provides a valid alternative to traditional approaches in atmospheric equilibrium gas-aerosol partitioning modeling which are based on chemical potentials and inferred activity coefficients. The traditional solution algorithms require computationally comprehensive online or offline iterations (E-AIM and ISORROPIA-II, respectively) to compute the equilibrium composition of compounds in the solution.

The  $\nu_w$ -concept allows the gas/liquid/solid equilibrium partitioning of single or multiple charged electrolytes, including semi- or non-volatile compounds and partial dissociation of bi-sulfates, to be computed analytically, since the stoichiometric coefficient of water ( $\nu_w$ ) contains a priori information of the water activity as it is based only on the solute solubility and effective solute dissociation. Furthermore, the successful application

### Derivation of the stoichiometric coefficient of water

S. Metzger et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

to mixed solutions may give insights into the basis of the so-called ZSR-relationship Zdanovskii-Stokes-Robinson (Stokes and Robinson, 1966), a widely used method in atmospheric modeling (including E-AIM and ISORROPIA2) to derive the water content of mixed solutions from the corresponding binary solutions upon the application of empirical mixing rules.

Finally we note that the  $v_w$ -concept of ML07 goes back to Arrhenius' theory of partial dissociation (Arrhenius, 1887; Heyrovska, 1989), and van't Hoff's gas-solution analogy originally used to explain osmosis (van't Hoff, 1887). Interestingly, the work by van't Hoff on osmosis was initially disputed until Lord Rayleigh (1897) put van't Hoff's arguments on a firmer ground. One issue at that time was that Gibbs (1897) proposed an alternative analysis of the osmotic pressure in terms of chemical potentials, which has subsequently served as an essential element of textbooks about osmosis. Van't Hoff's and Rayleigh's original ideas were then disregarded in favor of theories making use of the Gibbs free energy and of chemical potentials. However, these theories must be considered as equivalent in treating osmosis, and they do not provide the benefits of generality and rigor (<http://urla.tripod.com/evidence.htm>). Thus, based on the original ideas of Arrhenius, van't Hoff and Rayleigh,  $v_w$  builds on the concept of osmosis, analogously to the stoichiometric coefficients for solutes, to account on a molar basis for the amount of water consumed by hydration.

## Appendix A

### Clarification of the EQSAM3 concept (ML07)

EQSAM3 solves the gas-liquid-solid partitioning analytically and non-iteratively upon calculation of the single solute concentrations from the compound's solubility and a newly introduced variable; the stoichiometric coefficient of water,  $v_w$ . This is a different approach compared to other equilibrium models, and previous EQSAM versions

## Derivation of the stoichiometric coefficient of water

S. Metzger et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



(EQSAM, Metzger et al., 2002; EQSAM2, Metzger et al., 2006). The source code of EQSAM3 is available on request.

ML07 introduced  $\nu_w$  to represent the degree to which water is consumed or bound in processes such as solvation, hydration, hydrolysis or similar other processes that consume water and which are associated with a chemical reaction. These processes are, apart from some exceptions (such as water chemically bound in minerals), usually neglected in the stoichiometrical notation of chemical reactions in solution, and hence, activity coefficients are needed. Instead, EQSAM3 does not require activity coefficients for non-volatile aqueous compounds. The use of  $\nu_w$  allows ML07 to determine the amount of water associated with a dissolved solute without the use of activity coefficients.

EQSAM3 is based on 5 key equations, all of which are detailed in ML07, but a summary of each equation is given here for completeness. These equations are used to calculate:

1. The stoichiometric coefficient of water
2. The single solute molality (as a function of RH)
3. The aerosol associated water mass (water uptake)
4. The relative humidity of deliquescence (of single and mixed solutes)
5. Activity coefficients (for semi-volatile species)

These 5 key equations are outlined in this section.

## A1 Stoichiometric coefficient of water

EQSAM3 calculates the single solute concentrations from the compound's solubility and a newly introduced variable; the stoichiometric coefficient of water,  $\nu_w$ . ML07 introduced a relation for the dependence of  $\nu_w$  on the solubility:

$$\nu_w = \nu_{w,0} + \log(2/\nu_e \times 1000w_s), \quad (\text{A1})$$

## Derivation of the stoichiometric coefficient of water

S. Metzger et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## Derivation of the stoichiometric coefficient of water

S. Metzger et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

with  $w_s$  the solubility mass fraction, defined as mass of solute per total mass of the solution and with  $v_{w,0}=-1$  indicating that each mole of solute “consumes”  $\log_{10}\left(\frac{2}{v_e} \times 1000 w_s\right)$  moles of initially “free” water. Note that Eq. (A1) can be expressed in terms of an  $\pm$ -ion-pair and the natural logarithm as:

$$v_w^\pm = v_{w,0}^\pm + \log\left(\frac{2}{v_e} \times w_s\right) = v_{w,0}^\pm + \ln\left(\frac{2}{v_e} \times w_s\right) / \ln(10), \quad (\text{A2})$$

with  $v_{w,0}^\pm=2$  instead of  $v_{w,0}=-1$ , as it is derived in Sect. 2 from first principles.

## A2 Single solute molality as a function of RH (water activity)

The introduction of the coefficient  $v_w$  allows generalization of the solute mole fraction and molality, which can be related to the solubility (ML07). Using the generalized mole fraction instead of the (traditional) mole fraction has the advantage that we can directly express the single solute molality (of non-volatile compounds) as a function of RH without considering activity coefficients. In contrast, the (traditional) mole fraction and molality need to be corrected by activity coefficients to match measurements. The generalized mole fraction does not need such corrections.

The generalized mole fractions for solute and water at equilibrium are respectively expressed as

$$\tilde{x}_s = v_e n_s / [v_w n_w + v_e n_s], \quad (\text{A3a})$$

$$\tilde{x}_w = v_w n_w / [v_w n_w + v_e n_s]. \quad (\text{A3b})$$

Equation (A3a, b) differ from their traditional definitions  $x_s = n_s / [n_w + n_s]$  and  $x_w = n_w / [n_w + n_s]$  only by the effective stoichiometric coefficients for the solute  $v_e$  and water  $v_w$  which account for solution non-ideality by partial or complete dissociation;  $n_s$  is the number of moles of solute that is dissolved in a solution with  $n_w$  the moles of solvent water.



In accord with the traditional definition the sum of the generalized mole fractions yields unity, i.e. for a binary solution (one solute and water):

$$\tilde{x}_s + \tilde{x}_w = 1. \quad (\text{A3c})$$

The activity of water in terms of the generalized mole fraction for water at equilibrium is

$$a_w = \tilde{x}_w = \text{RH}, \quad (\text{A4a})$$

which can be expressed as

$$\tilde{x}_w = v_w n_w / [v_w n_w + v_e n_s^o] = 1 / [1 + v_e n_s^o / v_w n_w] = \text{RH}, \quad (\text{A4b})$$

and upon rearranging

$$n_s^o / n_w = v_w / v_e \cdot (1/\text{RH} - 1), \quad (\text{A5})$$

The single solute molality,  $m_{ss}$ , is defined as the moles of solute per kilogram water, i.e.

$$m_{ss} = 1000[\text{g}(\text{H}_2\text{O})]/M_w [\text{g/mol}] \cdot n_s^o [\text{mol}]/n_w [\text{mol}] = 55.51 n_s^o / n_w [\text{mol/kg}(\text{H}_2\text{O})], \quad (\text{A6})$$

where  $55.51/n_w$  denotes the number of moles of water per kilogram and  $M_w=18.015[\text{g/mol}]$  is the molar mass of water;  $n_s^o$  denotes the initial number of moles that effectively dissociates into  $v_e n_s^o$  number of moles at equilibrium (saturation). Thus, the initial and non-equilibrium single solute molality,  $m_{ss}^{v_s^o} = n_s^o / n_w \cdot 55.51$  (with  $v_s^o=1$ ) yields at equilibrium the saturation molality  $m_{ss,\text{sat}}^{v_e/v_w} = v_e / v_w n_s^o / n_w \cdot 55.51$ , or the actually measured saturation activity,  $a_{s,o}^{v_s^o} = a_{w(\text{hyd}),\text{sat}} = a_{ss,\text{sat}}^{v_e/v_w}$ , with  $n_s^o / n_w = m_{ss}^{v_s^o} / 55.51 \Rightarrow v_e / v_w n_s^o / n_w = m_{ss,\text{sat}}^{v_e/v_w} / 55.51$ . Note that if  $v_e / v_w \neq 1$  the units for the solute molality in these equations would not be balanced in the traditional and chemical potential based approaches, but this is ignored in this model.

**Derivation of the stoichiometric coefficient of water**

S. Metzger et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## Derivation of the stoichiometric coefficient of water

S. Metzger et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Substitution in Eq. (A5) yields, by considering that

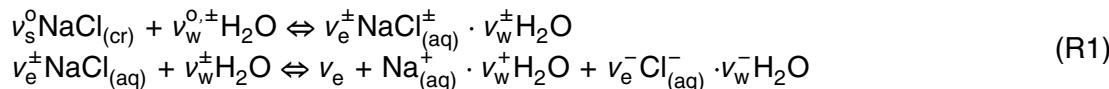
$$n_s^0/n_w = m_{ss}^{v_s^0}/55.51 \Rightarrow m_{ss,sat}^{v_e/v_w}/55.51 = v_w/v_e \cdot (1/RH - 1), \quad (A7)$$

so that we can express Eq. (A6) in terms of RH and the effective stoichiometric coefficients for the solute  $v_e$  and water  $v_w$ , i.e.

$$m_{ss,sat} = [v_w/v_e \cdot 55.51 \cdot (1/RH - 1)]^{v_w/v_e}. \quad (A8)$$

Equation (A8) is the basic formulation of ML07 (their Eq. 20) from which all further equations used in EQSAM3 can be expressed as a function of RH,  $v_e$  and  $v_w$ .

Note that  $m_{ss,sat}^{v_e/v_w}$  directly follows from the example reaction:



when we explicitly include water. Considering only the dissolution of a pure compound, which potentially dissociates effectively (either partly or completely) into  $v_e^+$  cations and  $v_e^-$  anions, with  $v_e^{\pm} = v_e^+ + v_e^-$ , a certain amount  $v_w^{\pm} = v_w^+ + v_w^-$  of water will be stoichiometrically consumed by (or bound to) the solute that drives the dissolution and potential dissociation. Since the dissolution and potential dissociation does not change the initial amount of the solute (no chemical reaction), and since the amount of water consumed is associated with the solute (or its ions), the associated concentration of the water bound to the solute must equal the hydrated solute concentration (both relative to the free water), so that with  $a_{s,0}^{v_s^0} = a_{w(\text{hyd}),\pm} = a_{s,\pm}^{v_e^{\pm}/v_w^{\pm}}$  as above.

Thus, the concentration at equilibrium (after dissolution and potential dissociation) is higher by the exponent  $v_w^{\pm}/v_e^{\pm}$  than the initial solute concentration  $a_s^{v_s^0} = 55.51 v_s^0 n_s^0 / (v_w^0 n_w)$  (not being in equilibrium), with  $v_s^0 = 1$  and  $v_w^0 = 1$  for the stoichiometrical notation (which is usually neglected). Or in other words, the amount of water bound to the solute decreases the amount of remaining “free” water in the solution so

## Derivation of the stoichiometric coefficient of water

S. Metzger et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



that the amount of  $v_s^0 v_e^\pm = v_s^0 (v_e^+ + v_e^-)$  dissolved and potentially dissociated solute “sees” a reduced water activity by the exponent  $v_w^\pm / v_e^\pm$ , i.e.  $a_{s^\pm}^{v_s^\pm / v_w^\pm} = 55.51 v_s^\pm n_s^0 / (v_w^\pm n_w^\pm)$ , with  $n_s^0$  always dissolved in 1 l of solution (for the molarity scale), or 1000 g of water (for the molality scale), i.e.  $n_w^0 = 1000[\text{g}] / 18.015[\text{g/mol}] = 55.51[\text{mol}]$ .  $n_w$  denotes the number of moles of “free” water for the initial solution containing  $v_s^0 n_s^0$  moles of solute,  $n_w^\pm$  denotes the number of moles of “free” water for the saturated solution (at equilibrium) containing actually  $v_s^0 v_e^\pm n_s^0$  moles of solute, but with  $n_w^\pm = n_w^0 - n_w^\pm$  fewer moles of “free” water  $n_w^\pm$ .

### A3 Aerosol water mass (water uptake)

The water mass associated with a single solute in an atmospheric aerosol is calculated from Eq. (A8) by:

$$m_{w,\text{sat}} = n_s / m_{ss,\text{sat}} = n_s / (v_w / v_e \cdot 55.51 \cdot (1/\text{RH} - 1))^{v_w / v_e}, \quad (\text{A9})$$

Equation (A9) equals Eq. (22) of ML07;  $m_{w,\text{sat}}$  is the water mass associated with  $n_s$  moles of dissolved single solute in a saturated aerosol phase. The total mass of water in an aerosol is then obtained by adding up the (partial) water masses (obtained from Eq. (A9)) of all solutes dissolved in the aqueous phase, but only for compounds those RH is above the compound’s relative humidity of deliquescence (RHD).

#### A3.1 Relative humidity of deliquescence of single solutes (single solutions)

The RHD of a compound can be calculated using Eq. (A8) if the single solute molality at saturation ( $m_{ss,\text{sat}}$ ) is used that can be e.g. directly obtained from the solubility mass fraction, i.e.  $m_{ss,\text{sat}} = 1000 / M_s / (1/w_s - 1)$ . Rearranging Eq. (A8) and solving for RHD, gives the expression:

$$\text{RHD} = \left( v_e / v_w \cdot m_{ss,\text{sat}}^{v_e / v_w} / 55.51 + 1 \right)^{-1}, \quad (\text{A10})$$

with  $55.51[\text{mol/kg}(\text{H}_2\text{O})]$ . Equation (A10) equals Eq. (21) of ML07. Tables of RHD calculated using this formula compared to measurements are given in ML07.

### A3.2 Relative humidity of deliquescence of mixed solutes (mixed solutions)

The MRHD that corresponds to a mixed solution is inferred from the same equations used to derive the RHD of single solutes, i.e. (A10) (or Eq. 21 and Sects. 4.1.5 and 4.1.9 of ML07) by using the mean values of the relevant thermodynamic properties, i.e. the effective stoichiometric coefficients of the solutes ( $\bar{\nu}_e$ ) and water ( $\bar{\nu}_w$ ) of all single solutes in the mixed solution, their solubilities and molar masses need to derive the mean molality at saturation ( $\bar{m}_{ss,sat}$ ).

$$\text{MRHD} = (\bar{\nu}_e / \bar{\nu}_w \cdot \bar{m}_{ss,sat}^{\bar{\nu}_e / \bar{\nu}_w} / 55.51 + 1)^{-1}, \quad (\text{A11})$$

### A4 Activity coefficients

In EQSAM3 activity coefficients are not needed for non-volatile species, but they are required for the calculation of the gas-aerosol partitioning of semi-volatile species. The mean ion pair activity coefficient,  $\gamma_s^\pm$ , of a volatile compound is obtained by substitution of the single solution molality, i.e. Eq. (A8), into Eq. (14–16) of ML07. Note that according to ML07 and as mentioned above, Eq. (14–16) yields unity for a pure compound dissolution (e.g. associated hydration but no chemical reaction), so that upon use of the standard definition of the activity i.e.,  $a_s^{V_s} = (m_{ss} \gamma_s^\pm)^{V_s}$  (Robinson and Stokes, 1965), we find, by accounting for the charge density of the solution,  $\xi_s$ , (Metzger et al., 2002) and the ratio of the water and solute density,  $\rho_w / \rho_s$

$$\gamma_s^\pm = \rho_w / \rho_s \cdot \left( \text{RH}^{-\nu_w / \nu_e} / [\nu_w / \nu_e \cdot 55.51 \cdot (1/\text{RH} - 1)]^{\nu_w / \nu_e} \right)^{2/\xi_s}. \quad (\text{A12})$$

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



*Acknowledgements.* This work was financed through the CIRCE Integrated Project – Climate Change and Impact Research: the Mediterranean Environment (<http://www.circeproject.eu/>) and supported by the European Commission's Sixth Framework Program, Sustainable Development, Global Change and Ecosystems, Project No. 036961. LX and JEP are grateful for the support of the NASA Glory Science Team under grant number NNX08AL83G as well as that from NASA JPL under contract number NM0710973. We thank T. Nenes for kindly providing the ISORROPIA-II source code and S. L. Clegg and A. S. Wexler for providing access to E-AIM via the Web interface <http://www.aim.env.uea.ac.uk/aim/aim.php>. We further thank K. Pringle and H. Tost for their support with the ongoing model development of EQSAM3, GMXe and their evaluation, and all contributors of the interactive discussions of ML07 and Xu et al. (2009) who have stimulated this work (<http://www.atmos-chem-phys.net/7/3163/2007/acp-7-3163-2007.html>) (<http://www.atmos-chem-phys-discuss.net/9/9551/2009/acpd-9-9551-2009-discussion.html>).

The service charges for this open access publication have been covered by the Max Planck Society.

## References

- Arrhenius, S.: Über die Dissociation des in Wasser Gelösten Stoffe, Z. Phys. Chem., 1, 631, 1887.
- Einstein, A.: Über die von der molecular kinetischen Theorie der Wärme geforderte Bewegung von in ruhenden Flüssigkeiten suspendierten Teilchen, Annalen der Physik, 17, Universität Wien, <http://www.zbp.univie.ac.at/dokumente/einstein2.pdf>, 1905.
- Fountoukis, C. and Nenes, A.: ISORROPIA II: a computationally efficient thermodynamic equilibrium model for  $K^+Ca^{2+}Mg^{2+}NH_4^+Na^+SO_4^{2-}NO_3^-Cl^-H_2O$  aerosols, Atmos. Chem. Phys., 7, 4639–4659, 2007, <http://www.atmos-chem-phys.net/7/4639/2007/>.
- Heyrovska, R.: A Reappraisal of Arrhenius' Theory of Partial Dissociation of Electrolytes, Am. Chem. Soc., 1989.
- Lord Rayleigh: The theory of solutions, Nature, 55, 253–254, 1897.

## Derivation of the stoichiometric coefficient of water

S. Metzger et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Derivation of the  
stoichiometric  
coefficient of water**

S. Metzger et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Metzger, S., Dentener, F.J., Lelieveld, J., and Pandis, S.N.: Gas/aerosol partitioning I: A computationally efficient model, *J. Geophys. Res.*, 107(D16), ACH 16-1-24, doi:10.1029/2001JD001102, 2002.

Metzger, S., Mihalopoulos, N., and Lelieveld, J.: Importance of mineral cations and organics in gas-aerosol partitioning of reactive nitrogen compounds: case study based on MINOS results, *Atmos. Chem. Phys.*, 6, 2549–2567, 2006, <http://www.atmos-chem-phys.net/6/2549/2006/>.

Metzger, S. and Lelieveld, J.: Reformulating atmospheric aerosol thermodynamics and hygroscopic growth into fog, haze and clouds, *Atmos. Chem. Phys.*, 7, 3163–3193, 2007, <http://www.atmos-chem-phys.net/7/3163/2007/>.

Pfeffer, W.: Osmotische Untersuchungen – Studien zur Zellmechanik, Engelmann, Leipzig, 1877.

Stokes, R. H. and Robinson, R. A.: Interactions in aqueous nonelectrolyte solutions, I. Solute-solvent equilibria, *J. Phys. Chem.*, 70, 2126–2130, 1966.

van 't Hoff, J. H.: Die Rolle des osmotischen Druckes in der Analogie zwischen Lösungen und Gasen, <http://urila.tripod.com/Hoff.pdf>, *Z. Phys. Chem.*, 1, 481–508, 1887.

van 't Hoff, J. H.: Zur Theorie der Lösungen', *Z. Phys. Chem.*, 9, 477, 1892.

van 't Hoff, J. H.: Osmotical pressure and chemical equilibrium, <http://nobelprize.org/nobel-prizes/chemistry/laureates/1901/hoff-lecture.pdf>), Nobel Lecture, 1901.

Wexler, A. S. and Clegg, S. L.: Atmospheric aerosol models for systems including the ions  $\text{H}^+$ ,  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{H}_2\text{O}$ , *J. Geophys. Res.*, 107(14), 4207, D14, 2002.

Xu, L., Penner, J. E., Metzger, S., and Lelieveld, J.: A comparison of water uptake by aerosols using two thermodynamic models, *Atmos. Chem. Phys. Discuss.*, 9, 9551–9595, 2009, <http://www.atmos-chem-phys-discuss.net/9/9551/2009/>.

# Osmosis - Pfeffer cell

Integration boundaries

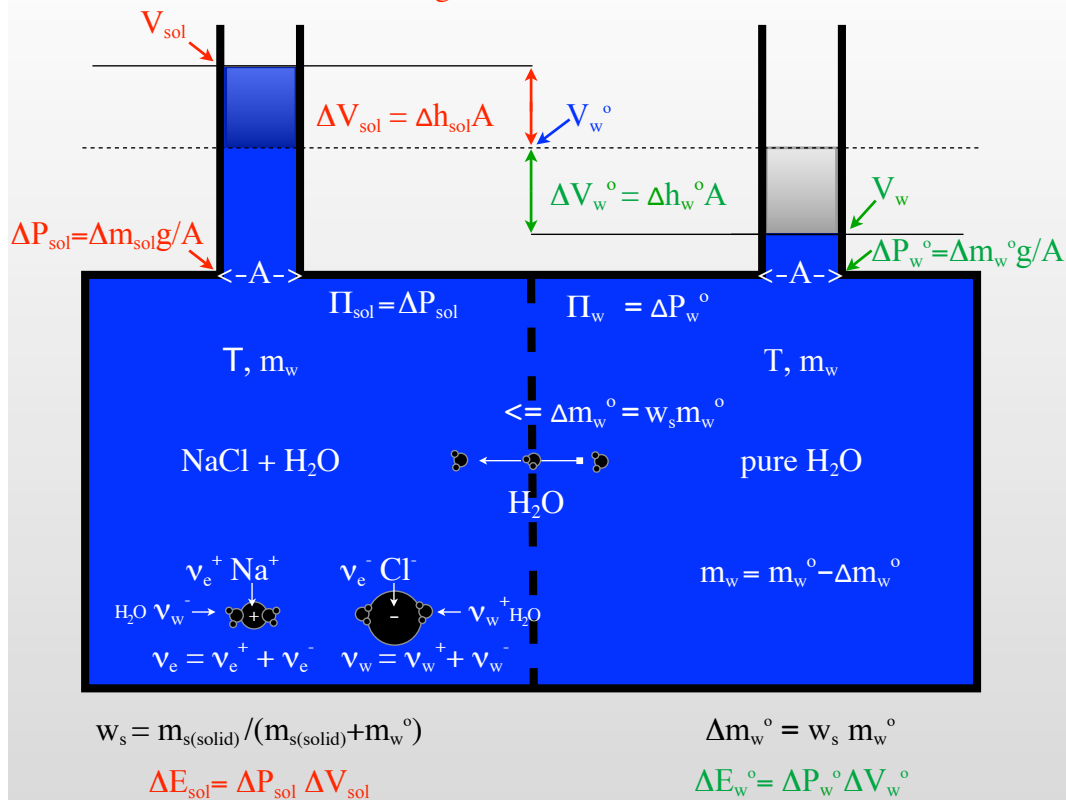


Fig. 1. Sketch of a Pfeffer cell: left compartment solution, right compartment pure water.

## Derivation of the stoichiometric coefficient of water

S. Metzger et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Derivation of the  
stoichiometric  
coefficient of water

S. Metzger et al.

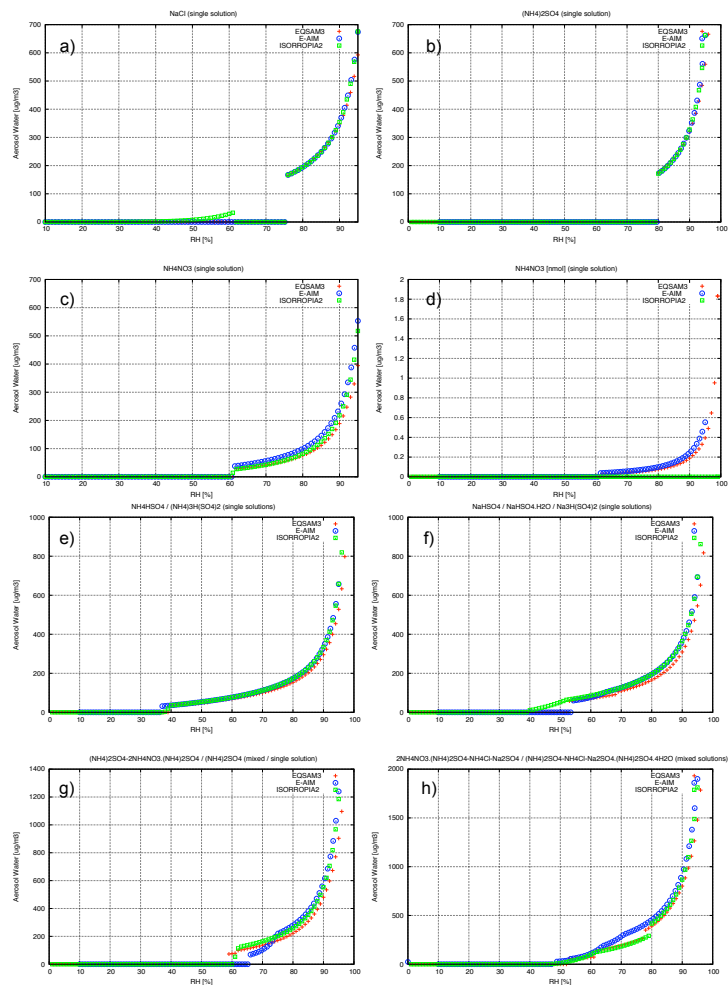


Fig. 2. Water uptake of atmospheric aerosols for various single and mixed salt solutions.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

