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**Reformulating
atmospheric aerosol
thermodynamics**

S. Metzger and
J. Lelieveld

Reformulating atmospheric aerosol thermodynamics and hygroscopic growth into haze and clouds

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Abstract

Modeling atmospheric aerosol and cloud microphysics is rather complex, even if chemical and thermodynamical equilibrium is assumed. We show, however, that the thermodynamics can be considerably simplified by reformulating equilibrium to include water, and transform laboratory-based concepts to atmospheric conditions. We generalize the thermodynamic principles that explain hydration and osmosis – merely based on solute solubilities. In chemical and thermodynamical equilibrium the relative humidity (RH) determines the saturation molality, including solute and solvent activities (and activity coefficients), since the water content is fixed by RH for a given aerosol concentration and type. As a consequence, gas/liquid/solid aerosol equilibrium partitioning can be solved analytically and non-iteratively. Our new concept enables an efficient and accurate calculation of the aerosol water mass and to directly link the aerosol hygroscopic growth to haze and cloud formation.

We apply our new concept in the 3rd Equilibrium Simplified Aerosol Model (EQSAM3). Its input is limited to the species' solubilities from which a newly introduced stoichiometric coefficient for water is derived. Analogously, we introduce effective stoichiometric coefficients for the solutes to account for complete or incomplete dissociation. We show that these coefficients can be assumed constant over the entire activity range and calculated for various inorganic, organic and non-electrolyte compounds, including alcohols, sugars and dissolved gases. EQSAM3 calculates the aerosol composition and gas/liquid/solid partitioning of mixed inorganic/organic multicomponent solutions and the associated water uptake for almost 100 major compounds. It explicitly accounts for particle hygroscopic growth by computing aerosol properties such as single solute molalities, molal based activities, including activity coefficients for volatile compounds, and deliquescence relative humidities of mixed solutes. Various applications and a model inter-comparison indicate that a) the application is not limited to dilute binary solutions, b) sensitive aerosol properties such as the pH of binary and mixed inorganic/organic salt solutions up to saturation can be computed accurately, and c)

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aerosol associated water is important for atmospheric chemistry, visibility, weather and climate.

1 Introduction

It is widely acknowledged that atmospheric aerosol particles affect human and ecosystem health, clouds and climate (e.g. EPA, 1996; Holgate et al., 1999; Seinfeld and Pandis, 1998; IPCC, 2001). It is less well recognized that gas/liquid/solid partitioning of atmospheric particles and precursor gases largely determine the composition and hygroscopicity of the aerosols, which in turn govern the size distribution, the atmospheric lifetime of both the particles and the interacting gases, and the particle optical properties. For instance, sea salt particles can deliquesce at a very low relative humidity (RH) of ~32% since they contain a small amount of the very hygroscopic salt magnesium chloride (MgCl_2). Therefore, marine air is often much hazier than continental air at the same ambient temperature (T) and RH.

Overall, the most abundant aerosol species is water. For a given T and RH aerosol water determines the phase partitioning between the gas-liquid-solid and ice phases and the composition of atmospheric aerosols due to changes in the vapor pressure above the particle surface (Pruppacher and Klett, 1997). The hygroscopic growth of the aerosol particles influences heterogeneous reactions, light extinction and visibility. Aerosol water depends, besides the meteorological conditions, on the ionic composition of the particles, which in turn depends on the aerosol water mass. Consequently, gas-aerosol partitioning and aerosol water mass are difficult to measure or predict numerically (by established methods), even if the complex gas-aerosol system is simplified by assuming thermodynamic gas/aerosol equilibrium (Seinfeld and Pandis, 1998).

The underlying principles that govern the gas-aerosol equilibrium partitioning and hygroscopic growth have been formulated toward the end of the nineteenth century by Gibbs (1839–1903), the architect of equilibrium thermodynamics. Most of our current understanding of equilibrium, which follows from the second law of thermodynamics,

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derives from Gibbs (1876). Among the numerous publications that have appeared since, none has attempted to transform the basic principles of equilibrium thermodynamics to atmospheric aerosol modeling applications.

The conceptual difficulty has been that the water mass, used to define the aerosol activity, was kept constant, which is reasonable for laboratory but not for atmospheric conditions. Aerosol water depends for a given amount and type of solute also on thermodynamics, i.e. on RH. And since RH depends on ambient water vapor and the strongly temperature dependent saturation water mass, aerosol thermodynamics and cloud microphysics are directly coupled. The aerosol water mass is determined by the aerosol composition (hygroscopicity), i.e. the amount of solute that dissolves for a given amount of dry aerosol mass at a given RH, as well as the available water vapor mass.

Under subsaturated conditions, i.e. $RH < 1$, the aerosol water mass is limited by the available water vapor mass. Under saturated and supersaturated conditions, i.e. $RH > 1$, the aerosol water mass is limited by the saturation water mass. Excess water vapor directly condenses into cloud droplets or, at a sufficiently low temperature, into ice crystals. The freezing point depression is determined by the dissolved aerosol mass, i.e. by the amount of solute by which the type of solute determines the amount that dissolves. Here we show that all relevant properties such as dry and ambient radii, mass and number distribution can be directly derived at a given RH, and subsequently also the initial cloud water/ice mass, cloud droplet/ice number concentrations, and the cloud cover. Our method is more explicit than the traditional concept of cloud condensation nuclei (CCN), which relies on arbitrary activation thresholds, and does not directly relate the particle chemical composition to droplet formation.

Overcoming the conceptual difficulty mentioned above has several advantages. First, the complex system of the gas/liquid/solid aerosol equilibrium partitioning can be solved analytically, which limits computational requirements. Second, a large number of aerosol physical-chemical properties can be directly and explicitly computed. This includes aerosol activities (including activity coefficients), the water activity (with or without the Kelvin term), single solute molalities of binary and mixed solutions of inor-

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ganic or mixed inorganic/organic solutions, relative humidities of deliquescence (RHD) of soluble salt compounds (single or mixed solutes), and related optical properties. Third, our new concept allows to consistently and efficiently link aerosol thermodynamics to cloud microphysics through explicit computation of the aerosol water mass.

5 Fourth, the account of aerosol chemical composition enables a direct connection with emission sources, being characterized by a certain mix of chemical compounds. Thus the emissions can be explicitly linked to atmospheric conditions, including visibility reduction and climate forcing through anthropogenic activities. It abandons the use of ambiguous terms such as “marine” and “continental” aerosols, and refines lumped categories such as mineral dust, biomass burning, sea salt, organic and sulfate aerosols
10 currently used in atmospheric modeling.

In Sect. 2 we translate the basic thermodynamic principles of hydration and osmosis to atmospheric conditions. In Sect. 3 we derive the formulations required to calculate the aerosol activity (including solute molalities and activity coefficients)
15 and the aerosol associated water mass, and we demonstrate how the aerosol and cloud thermodynamics can be simplified by reformulating chemical equilibrium to include water. In Sect. 4 we apply these formulations in our EQUilibrium Simplified Aerosol Model, version 3 (EQSAM3), and present some selected first applications. Section 5 presents a discussion and Sect. 6 the conclusions. In an appendix,
20 available as electronic supplement (<http://www.atmos-chem-phys-discuss.net/7/849/2007/acpd-7-849-2007-supplement.zip>), we provide some background information, physical-chemical definitions and a complete set of figures of thermodynamic calculations of all species included in this study.

2 Thermodynamic principles

25 Equilibrium thermodynamics of atmospheric aerosols have – thus far – been defined for laboratory conditions and subsequently applied to atmospheric modeling, which introduces a conceptual difficulty. In contrast to the laboratory, water is not a constant in

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the atmosphere, and the available water mass depends primarily on the available water vapor (P_w [Pa]) and the temperature dependent saturation vapor pressure ($P_{w,sat}$ [Pa]); the ratio defines the relative humidity ($RH=P_w/P_{w,sat}$). Furthermore, the aerosol water mass depends on the hygroscopicity of the solute. In particular the hygroscopicity of salt solutes causes hygroscopic growth of aerosol particles at subsaturated atmospheric conditions ($RH<1$).

Near saturation or at supersaturation ($RH\geq 1$) the hygroscopic growth of aerosol particles continues to yield cloud droplets, whereby larger particles grow dynamically at the expense of smaller particles. However, at equilibrium, the water uptake of atmospheric aerosols is then only limited by $P_{w,sat}$ instead of P_w as it is the case of subsaturation. In either case the water uptake is also determined by the amount and type of solutes. In the laboratory this can be shown by the vapor pressure reduction after dissolving a salt solute in water, known as Raoult's law (Raoult, 1888). Note that Raoult's law characterizes the solvent and Henry's law the solute. However, in the atmosphere at equilibrium conditions, where evaporation balances condensation, the vapor pressure reduction is compensated by the associated water uptake.

2.1 Laboratory conditions

2.1.1 Osmosis

The nature of hygroscopic growth of solutes is best understood by using an osmotic system, represented by one solution separated from another by a semi-permeable membrane (Fig. 1a), as first investigated by Pfeffer (1881). Osmosis is the net flow of water through the membrane driven by a difference in solute concentrations, resulting in an osmotic pressure (turgor). The size of the membrane pores is large enough to let small particles (water molecules or small ions) pass freely, while the exchange of larger molecules (e.g. hydrated sodium and chloride ions) is inhibited.

Osmosis produces a pressure on a membrane, Π (in Pascal [$Pa=N/m^2$]), which depends primarily on the concentration of the solute, though also on its nature. Adding

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a salt solute to the left compartment of Fig. 1 – e.g. 1 mole of sodium chloride (NaCl) – develops an osmotic pressure due to the additional volume by the hydrated solute. Depending on the nature of the solute – in particular its chemical bond strengths – the salt solute can dissociate.

The osmotic pressure can be measured quantitatively from the hydrostatic pressure difference of either solute or solvent. The hydrostatic pressure can be regarded as an osmotic counter pressure. For water vapor the partial pressure changes above the two compartments yield $\Delta P_w^{(g)} = P_w^{(g)} - P_{w,o}^{(g)}$. Note that we consider osmotic pressure differences, since both compartments may contain solutes, so that the osmotic pressure difference $\Delta\Pi$ is composed of a) $\Delta\Pi_s$ for the solute, to account for the dissociation of the solute into ν_s moles, and b) $\Delta\Pi_w$ for water, to account for the volume increase due to the additional amount of water that causes hydration and dilution.

In equilibrium, evaporation and condensation of water molecules above each water surface balance, so that the pressure (difference) $\Delta P_w^{(g)}$ adjusts to a maximum, equal to the osmotic pressure difference, though with opposite sign ($\Delta P_w^{(g)} = -\Delta\Pi_w$). Although the magnitude of the molar pressure difference is characteristic for the solute, different solutes that occupy the same volume cause the same osmotic pressure (difference).

2.1.2 Gas-solution analogy

An important aspect of the osmotic pressure is that it directly relates aqueous and gas phase properties. For instance, for a closed system at equilibrium and constant temperature (T) the water vapor pressures above both compartments equal the corresponding osmotic pressures, i.e. $P_w^{(g)} = \Pi_w$ and $P_{w,o}^{(g)} = \Pi_{w,o}$, respectively. Since the total energy of the system must be conserved

$$\Delta G = P_w^{(g)} V^{(g)} - P_{w,o}^{(g)} V^{(g)} + \Pi V^{(aq)} - \Pi_o V^{(aq)} = 0. \quad (1)$$

For the gas phase we can express the energy terms ($P^{(g)} V^{(g)} [Pa][m^3] = [N/m^2][m^3] = [Nm] = [J]$) in terms of moles ($n^{(g)} [mol]$) with temperature

(T [K]), and invoke the gas law (with $R = 8.314$ [J/mol/K] the universal gas constant)

$$P_{w,o}^{(g)} V^{(g)} = n_{w,o}^{(g)} RT. \quad (2)$$

Similarly, we obtain for the aqueous phase

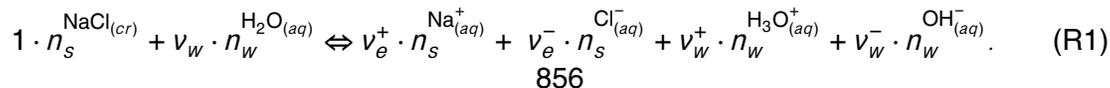
$$\Pi_{w,o} V^{(aq)} = n_{w,o} RT. \quad (3)$$

Note that the gas-solution analogy was noted and used by van 't Hoff and Ostwald about half a decade after Pfeffer's investigations to interpretate the osmotic pressure (van 't Hoff, 1887). Together with Arrhenius' theory of partial dissociation of electrolytes in solutions (Arrhenius, 1887), the principles of osmosis can be explained, provided that the water consumed for hydration is consistently accounted for.

2.1.3 Hydration

The osmotic pressure is caused by the hydration of n_s moles of solute. The hydration "consumes" water, which leads to a change in volume. For an equilibrium system any change in volume needs to be compensated, resulting in water uptake. The volume changes because of a) the additional volume of solute, by which the solute partly or completely dissociates due to hydration, b) due to the volume of water that is "consumed" by the hydration, and c) the chemical restructuring of the solute and water molecules. For some hygroscopic solutes, such as e.g. magnesium chloride ($MgCl_2$), this restructuring can even lead to a volume depression, since the entropy of the hydrated magnesium chloride ions is smaller than that of the crystalline salt, and the hydrated $MgCl_2$ ions have a higher structural order that occupies less volume.

Strong electrolytes such as $NaCl$ or $MgCl_2$ dissociate practically completely due to hydration. The chemical dissociation of e.g. sodium chloride ($NaCl$) (see example given in Fig. 1a) involves water that is consumed by the hydration processes, for which we formulate the equilibrium reaction



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The subscript “ e ” denotes the stoichiometric coefficients that account for effective dissociation ($v_e = v_e^+ + v_e^-$). For strong electrolytes they equal the stoichiometric coefficients for complete dissociation ($v_s = v_s^+ + v_s^-$). The stoichiometric coefficients express the minimum number of moles of each reaction component that is needed to form one mole of compound. NaCl dissociates into two moles ($v_e = 2$), i.e. one mole of NaCl yields one mole ($v_e^+ = 1$) of sodium (Na^+) and one mole ($v_e^- = 1$) of chloride (Cl^-). The solute hydration is associated with the consumption of a certain number of moles of water. We therefore also introduce a stoichiometric coefficient for the solvent (water), $v_w = v_w^+ + v_w^-$, to account for the actual number of moles of solvent (water) needed for the solvation (hydration) and solute dissociation.

In Fig. 1a the solution (left compartment) contains “water-binding” particles, and its volume expands at the expense of the right compartment due to water consumption. In case of a closed system the total aqueous ($V^{(aq)}$) and gaseous ($V^{(g)}$) volumes remain constant. The differences in energy (left and right compartment) can thus be expressed in terms of moles of water

$$\Delta \Pi_w V^{(aq)} = (\Pi_w - \Pi_{w,o}) V^{(aq)} = v_w n_w RT. \quad (4a)$$

Similar to Eq. (4a) we can express the energy contained in either of the compartments in terms of the number of moles of solute and solvent, so that for the solution (left compartment)

$$\Pi V^{(aq)} = (\Pi_{w,o} + \Delta \Pi_w) V^{(aq)} = (v_w n_w + v_e n_e) RT. \quad (4b)$$

2.1.4 Generalized mole fraction

The ratio of Eqs. (4a) and (4b) provides a very useful expression for the ratio of the osmotic pressure difference and the solution osmotic pressure

$$\Delta \Pi_w / \Pi = v_w n_w / (v_w n_w + v_e n_e) = \tilde{\chi}_w, \quad (5)$$

$\tilde{\chi}_w$ yields the generalized mole fraction of water, while the mole fraction of water is defined as $\chi_w = n_w / (n_w + n_s)$; accordingly the solute mole fraction is $\chi_s = n_s / (n_w + n_s)$, by which the sum over the mole fractions is unity, i.e. $\chi_s + \chi_w = 1$.

Note that Eq. (5) involves the following relations:

- 5 $-\Delta\Pi = \Delta\Pi_w + \Delta\Pi_s \Rightarrow \Delta\Pi_w = \Delta\Pi - \Delta\Pi_s,$
- $-\Delta\Pi = \Pi - \Pi_o$ with $\Pi = \Pi_w + \Pi_s$
- $-\Delta\Pi_s = \Pi_s - \Pi_{s,o}$ with $\Pi_{s,o} = 0$
- $-\Delta\Pi_w = \Pi_w - \Pi_{w,o}$ with $\Pi_{w,o} = \Pi_o$
- $-\Delta\Pi_w / \Pi = \Pi_w / \Pi = -\Pi_s / \Pi = 1 - \tilde{\chi}_s$

10 with $\tilde{\chi}_s$ denoting the generalized mole fraction of the solute, with $\tilde{\chi}_s + \tilde{\chi}_w = 1$.

Equation (5) expresses the fraction of water required for hydration as the system compensates the vapor pressure reduction through a net flow of water from the right into the left compartment (Fig. 1a). For an osmotic (closed) system this results in a difference in water activity ($\Delta a_w^{(aq)} = a_{w,o}^{(aq)} - a_w^{(aq)}$), which, in equilibrium, equals a difference in relative humidity (ΔRH). Note that at equilibrium the osmotic pressure of the solute or solvent (in solution) equals the corresponding partial vapor pressure of solute or solvent above the solution, independent of the curvature of the surface. In contrast to the theoretical solvent partial pressure in solution, the (measurable) osmotic pressure is an effective pressure and hence implicitly accounts for any surface tension or non-ideality effects.

20 For an open system without a membrane the water uptake is the same because it only depends on the hygroscopic nature of the solute. However, the water activity remains constant, as it is fixed by RH. An atmospheric aerosol is an example of such an open system.

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2.2 Atmosphere

The principles of osmosis that explain the nature of hygroscopic growth of solutes in the laboratory also apply to atmospheric aerosols. However, at equilibrium in the atmosphere the vapor pressure reduction associated with the hydration of a solute is compensated by water uptake, as schematically shown in Fig. 1b. In contrast to controlled equilibrium conditions in the laboratory, with constant T , in the atmosphere RH also remains constant, provided that the water vapor concentration does not change due to the amount of condensing water vapor needed for hydration – a requirement that holds for tropospheric subsaturated conditions ($RH < 1$) – see cloud Sect. 4.3.2.

However, for atmospheric aerosols in equilibrium with ambient air the water activity is fixed by the available water vapor concentration and equals the fractional relative humidity ($a_w = RH$). Similar to the laboratory a solute specific molar amount of water is required for hydration, by which in this case the water needs to condense from the gas phase. Furthermore, since $a_w = RH = \text{const.}$ and no membrane separates solute and solvent, no hydrostatic counter pressure can build up. At equilibrium the vapor pressure reduction is therefore fully compensated by the associated water uptake of the water-binding solute(s)

$$\Delta P_w^{(g)} / P_w^{(g)} = 0. \quad (6)$$

The equilibrium condition further requires that the total change in energy is zero

$$\Delta G = \Delta \Pi \Delta V^{(aq)} = 0. \quad (7)$$

Changes in energy resulting from the hydration of the solute can, analogously to the laboratory, be expressed in terms of the effective numbers of moles of hydrated solute(s) and the total amount of water that drives hydration

$$\Delta \Pi V^{(aq)} = v_e \Delta n_s R T + v_w \Delta n_w R T. \quad (8)$$

Since $\Delta \Pi = 0$, we can rewrite Eq. (8)

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

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or analogously to Eq. (5), if divided by the osmotic pressure energy of the solution

$$v_e \Delta n_s / (v_w n_w + v_e n_s) = -v_w \Delta n_w / (v_w n_w + v_e n_s), \quad (10)$$

by which the difference in the amount of solute ($v_e \Delta n_s$) again causes a difference in water activity (Δa_w) – equal to a difference in relative humidity (ΔRH) – but compensated by the associated water uptake ($-v_w \Delta n_w$), so that a_w and RH remain unchanged. Note that the rhs of Eq. (10) equals Eq. (5) with respect to the reference condition, where $n_{s,0} = n_{w,0} = 0$ and $\Delta n_w = n_w - n_{w,0}$ and $\Delta n_s = n_s - n_{s,0}$, and that the water activity is defined as the ratio of the fugacity (the real gas equivalent of an ideal gas's partial pressure) of the water to its fugacity under reference conditions, but usually approximated by the more easily determined ratio of partial pressures.

3 Reformulating equilibrium thermodynamics

The “classical” treatment of equilibrium thermodynamics of atmospheric aerosols (see e.g. the electronic supplement <http://www.atmos-chem-phys-discuss.net/7/849/2007/acpd-7-849-2007-supplement.zip> for a summary) can be reformulated to consistently include water. For instance, from Eqs. (9) and (10) it follows that the water needed for hydration is directly proportional to the amount of solute, determined by the solute specific constants v_e and v_w , independent of the solute concentration. This has important implications because these constants enable the calculation of the single solute molalities from which the solute specific water uptake and derived properties can be calculated as a function of RH, v_e and v_w for binary and mixed solutions.

3.1 Solubility constants

Molality is a measure of solubility. At equilibrium the solution is saturated so that it contains the maximum concentration of ions that can exist in equilibrium with its solid (crystalline) phase. The amount of solute that must be added to a given volume of

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solvent to form a saturated solution is called the solubility of the solute. At equilibrium the ion product equals the solubility product constant (K_{sp}) for the solute. For instance, using the equilibrium constant for Reaction (R1) and including water

$$K_{\text{NaCl}(cr)} \cdot K_{\text{H}_2\text{O}(aq)} = [\text{Na}^+_{(aq)}]^{v_e^+} + [\text{Cl}^-_{(aq)}]^{v_e^-} + [\text{H}_3\text{O}^+_{(aq)}]^{v_w^+} + [\text{OH}^-_{(aq)}]^{v_w^-}, \quad (\text{K1})$$

5 with the equilibrium constant $K_{\text{H}_2\text{O}(aq)} = [\text{H}_3\text{O}^+_{(aq)}]^{v_w^+} + [\text{OH}^-_{(aq)}]^{v_w^-}$.

In terms of activities we can express (K1) as

$$K_{\text{NaCl}(cr)} \cdot K_{\text{H}_2\text{O}(aq)} = a_s^{v_e} \cdot a_w^{v_w} = a_{\text{Na}^+}^{v_e^+} \cdot a_{\text{Cl}^-}^{v_e^-} \cdot a_{\text{H}_3\text{O}^+}^{v_w^+} \cdot a_{\text{OH}^-}^{v_w^-} = 1. \quad (\text{K2})$$

The subscript “s” denotes the solute activity of the \pm -ion pair,

$a_{\text{NaCl}^\pm}^{v_e^\pm} = a_s^{v_e} = a_{\text{Na}^+}^{v_e^+} \cdot a_{\text{Cl}^-}^{v_e^-}$. Similarly the subscript “w” denotes the activity of water, i.e. the

10 water activity $a_{\text{H}_2\text{O}^\pm}^{v_w^\pm} = a_w^{v_w} = a_{\text{H}_3\text{O}^+}^{v_w^+} \cdot a_{\text{OH}^-}^{v_w^-}$. The subscripts for corresponding stoichiometric constants „+“ and “-“ denote cations and anions, respectively, and the subscript “e” denotes that stoichiometric constants must be used that account for an effective dissociation.

In the atmosphere the water activity is fixed by the relative humidity (Sect. 2.2). Furthermore, at equilibrium the total change in energy (associated with the hydration process) is zero ($dG=0$). Since this requirement must also hold for the reference condition with respect to temperature and pressure (i.e. the standard state), the summation over

the partial Gibbs free energies ($\sum_{i=1}^k v_{ij} g_{ij}^0$) is zero; if extended to include water

$$v_e g_s^0 + v_w g_w^0 = 0. \quad (11)$$

20 The equilibrium condition is fulfilled for a certain relation between the stoichiometric constants of water (v_w) causing the hydration of the v_e moles of solute, satisfying Eq. (11)

$$v_w = -v_e g_s^0 / g_w^0. \quad (12)$$

This relation between v_w and v_e , however, requires that the product of activities becomes unity when water is included (see e.g. the electronic supplement <http://www.atmos-chem-phys-discuss.net/7/849/2007/acpd-7-849-2007-supplement.zip> for a definition of equilibrium constants) so that the product of the equilibrium constants (K2) becomes unity. The general formulation of K2 for the j -chemical reaction is

$$K_{sp,j} = \exp\left(-1/RT \sum_{i=1}^k v_{ij} g_{ij}^o\right) = a_{s,j}^{v_{e,j}} \cdot a_{w,j}^{v_{w,j}} = 1. \quad (13)$$

Consistent with Eqs. (9) and (10) (by dropping the index j)

$$a_s^{v_e} = a_w^{-v_w}, \quad (14)$$

with $K_{\text{NaCl}(cr)} = K_{\text{H}_2\text{O}(aq)}^{-1}$ (K2). At equilibrium the energy gain associated with the dissolution/dissociation of a salt solute must be compensated for by the energy associated with hydration and dissociation of water. For charged species, for which the electrical forces must be considered, the potential for an electrochemical reaction is zero at equilibrium in case of electro-neutrality (Nernst, 1889) – a condition that is generally fulfilled for neutralization reactions, which includes the hydration of salt solutes.

3.2 Aerosol activities

In general, if the ion product of a solute deviates from the solubility product constant for the solute, the system is not in equilibrium, but it can rapidly adjust according to Le Chatelier's principle, and the reaction re-equilibrates after the excess ions precipitate or dissolve until the ion product deficit is compensated. The solubility product constant for a saturated binary solution (one solute and solvent), however, requires that v_e^+ cations be released for v_e^- anions, and at equilibrium

$$a_{s+}^{v_e^+} = a_{s-}^{v_e^-} = a_{w+}^{-v_w^+} = a_{w-}^{-v_w^-}. \quad (15)$$

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Described in terms of molality (moles of solute per kilogram solvent) $a_{s+}^{v_e^+}$ and $a_{s-}^{v_e^-}$ denote the activity of a solute (s) containing the cation (+) and anion (−) in solution; $a_{w+}^{-v_w^+}$ and $a_{w-}^{-v_w^-}$ denote the water activities. The molal solute activity is defined as

$$a_s^{v_e} = a_{s+}^{v_e^+} \cdot a_{s-}^{v_e^-} = (\gamma_{s+} m_{s+})^{v_e^+} \cdot (\gamma_{s-} m_{s-})^{v_e^-} = \gamma_s^{v_e} \cdot m_{s+}^{v_e^+} m_{s-}^{v_e^-} = (\gamma_s \cdot m_s)^{v_e}, \quad (16)$$

with $m_{s+}^{v_e^+}$, $m_{s-}^{v_e^-}$ and $m_s^{v_e}$ the cation, anion and solute molalities, respectively; $\gamma_{s+}^{v_e^+}$, $\gamma_{s-}^{v_e^-}$ and $\gamma_s^{v_e} = \left(\gamma_{s+}^{v_e^+} \cdot \gamma_{s-}^{v_e^-} \right)^{1/v_e}$ are the molal-scale activity coefficients of the cation, anion and the mean ionic activity coefficient of the solute, respectively; v_e^+ and v_e^- are their stoichiometric constants, i.e. the effective number of moles of cations and anions per mole dissociating solute (s), with $v_e = v_e^+ + v_e^-$. The aqueous single solute (ss) molality is defined as $m_{ss} = n_s / n_w$ [mol/kg H₂O], with n_s and n_w , the number of moles of solute and solvent (water), respectively; $1000/M_w = 55.51$ is the molal concentration of water.

3.3 Solubility

For a saturated binary solution, n_s and n_w can be directly determined from the solute solubility. The solubility can be expressed in terms of the saturation molality of the single solute, or as mass of solute per 100 gram of water, or mass percent W_s [%], i.e. mass of solute per total mass of solution (solute and solvent). For the latter

$$W_s = 100 \cdot w_s = 100 \cdot m_s / (m_s + m_w), \quad (17)$$

where $m_s = n_s M_s$ and $m_w = n_w M_w$ denote the mass in gram [g] of solute and solvent (water), respectively; M_s and M_w are the corresponding molar masses of solute and solvent with units gram per mole [g/mol].

At equilibrium a solution is saturated, i.e. it contains the maximum number of moles of solute that can be dissolved. This saturation number can be directly calculated from

the total mass of solution (with the total mass of solution fixed to 1000 gramm) from

$$n_s = 1000/M_s \cdot w_s, \quad (18a)$$

and the associated (free) number of moles of water of the solution from

$$n_w = 1000/M_w \cdot (1 - w_s). \quad (18b)$$

- 5 The molality is then related to the solute mass fraction by $m_{ss} = 1000/M_s \cdot 1/(1/w_s - 1)$.
The mass of hydrated solute can be expressed in terms of water by

$$\tilde{n}_w M_w = 1000 \cdot w_s, \quad (18c)$$

The relation between the moles of water is given by $\tilde{n}_w = n_{w,o} - n_w$, with $n_{w,o} = 55.51$ [mol].

10 3.4 Stoichiometric constant for water

The stoichiometric constant of water (ν_w) that hydrates ν_e moles of solute is related to ν_e according to Eq. (9) by $\nu_e \Delta n_s = -\nu_w \Delta n_w$. The term on the rhs expresses the amount of water required for the hydration of Δn_s moles of solute (where $\Delta n_w < 0$ since water is consumed), in equilibrium giving rise to an effective dissociation into ν_e moles.

- 15 Recalling that at equilibrium a binary solution is saturated for which the solubility product constant requires that ν_e^+ cations are released for ν_e^- anions, with the total of $\nu_e = \nu_e^+ + \nu_e^-$ ions of solute, and for which electroneutrality requires that accordingly ν_w^+ moles of $\text{H}_3\text{O}_{(aq)}^+$ and ν_w^- moles of $\text{OH}_{(aq)}^-$ (with $\nu_w = \nu_w^+ + \nu_w^-$) must be involved in the hydration of each mole of solute. Two moles of water are consumed for each mole of
- 20 $\text{H}_3\text{O}_{(aq)}^+$ and $\text{OH}_{(aq)}^-$ produced, and we express the stoichiometric constant of water as

$$\nu_w = \nu_{w,o} + \log(2 / \nu_e \cdot 1000 w_s), \quad (19)$$

with $1000w_s = \tilde{n}_w M_w$ according to Eq. (18c).

Table 1 lists the stoichiometric constants of water together with required thermodynamic data for nearly 100 compounds, including a) 7 major cations, i.e. hydrogen (H^+),

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ammonium (NH_4^+), sodium (Na^+), potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}) and iron (Fe^{2+} , Fe^{3+}), b) 14 major anions, i.e. phosphate (PO_4^{3-}), sulphate (SO_4^{2-}), hydrogen sulphate (HSO_4^-), nitrate (NO_3^-), chloride (Cl^-), bromide (Br^-), iodide (I^-), carbonate (CO_3^{2-}), hydrogen carbonate (HCO_3^-), hydroxide (OH^-), formate (CHO_2^-), acetate ($\text{C}_2\text{H}_3\text{O}_2^-$), oxalate ($\text{C}_2\text{O}_4^{2-}$), and citrate ($\text{C}_6\text{H}_5\text{O}_7^{3-}$), and c) 7 non-electrolytes, i.e. ammonia (NH_3), acetone ($(\text{CH}_3)_2\text{CO}$), methanol (CH_3OH), ethanol ($\text{CH}_3\text{CH}_2\text{OH}$), D-fructose ($\text{C}_6\text{H}_{12}\text{O}_6$), D-mannitol ($\text{C}_6\text{H}_{14}\text{O}_6$), sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$).

Note that v_w is fully determined by the solubility. For near-100% solubility v_w converges to 2 (theoretically to 2.301), while for less soluble solutes ($W_s \leq 10\%$) v_w approaches unity. For pure water v_w is not defined and not needed. $v_{w,0} = -1$ indicates that each mole of hydrated solute “consumes” $\log(2/v_e \cdot 1000 w_s)$ moles of water.

3.5 Single solute molality

The water uptake associated with hydration of a solute for a closed system (Fig. 1a) is the same as for an open system (Fig. 1b). According to Eq. (9) the water uptake is proportional to the amount of solute, whereby the relative amount of water is given by the mole fraction of water, and in terms of molality $m_{ss} = n_s/n_w \cdot 55.51$ [mol/kg H_2O]. The molality and the mole fraction of water are related by $x_w = n_w/(n_w + n_s) = 1/(1 + n_s/n_w) = 1/(1 + m_{ss}/55.51)$.

According to Eq. (5) the osmotic pressure difference for water $\Delta\Pi_w$ equals the osmotic pressure of water Π_w , so that at equilibrium the ratio of Π_w to the total osmotic pressure of the solution equals the relative humidity, i.e. $\Pi_w/\Pi = \text{RH}$. Since $\Pi_w/\Pi = \tilde{x}_w = 1/(1 + v_e n_s/v_w n_w)$, m_{ss} can be directly derived from RH if v_e and v_w are known

$$m_{ss} = \left[v_w/v_e \cdot 55.51 (1/\text{RH} - 1) \right]^{v_w/v_e}, \quad (20)$$

with transformation of n_s/n_w into molality (multiplication of both sides with $1000/M_w = 55.51$) and by considering that $m_{ss} \rightarrow m_{ss}^{v_e/v_w}$.

For four selected compounds from Table 1 Fig. 2a shows single solute molalities as a function of relative humidity (RH). Note that the full set of figures is presented in the electronic supplement (<http://www.atmos-chem-phys-discuss.net/7/849/2007/acpd-7-849-2007-supplement.zip>). RH equals the water activity (a_w). The single solute molalities include:

1. Measurements that are used in various thermodynamic equilibrium models (EQMs). Water activity data of NaNO_3 , Na_2SO_4 , NaHSO_4 , $(\text{NH}_4)_2\text{SO}_4$, $(\text{NH}_4)\text{HSO}_4$ from Tang and Munkelwitz (1994), NH_4NO_3 from Chan et al. (1992), KCl from Cohen et al. (1987). All other sources are given in Kim et al. (1993a, 1994b).
2. Measurements as listed in the CRC Handbook of Chemistry and Physics (2004–2005) (see footnote).
3. Calculations according to Eq. (20) using CRC-solubility measurements to derive v_w by assuming complete dissociation (v_s).
4. Same as (3) but using effective dissociation (v_e).
5. Estimates based on calculated solubility assuming that the solubility approximates one minus the ratio of initial molar volumes of water (V_w) and solute (V_s), i.e. $w_s = 1 - V_w/V_s$, with $V_w = M_w/\rho_w$ and $V_s = M_s/\rho_s$, where ρ_w and ρ_s denote the density of water and solute with units in gram per cubic centimeter [g/cm^3], respectively.

Figure 2a shows that Eq. (20) based on v_e is in excellent agreement with the measurements that are used in various EQMs, e.g. ISORROPIA (Nenes et al., 1998) and SCAPE (Kim et al. 1993ab, 1995), SCAPE2 (Meng et al., 1995), as previously used by Metzger et al. (2006), and with inferred measurements from the CRC Handbook. The single solute molalities plotted against RH start from saturation water activity, i.e. the relative humidity of deliquescence (RHD), until water vapor saturation, i.e. (RH=1).

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Note that usually the single solute molalities are plotted against water activity which in this case equals the RH. For all cases where water activity data from SCAPE2 were available also RHD values were derived. For all other cases, the single solute molalities are plotted over the entire RH range and only for some compounds a comparison with the inferred CRC measurements is possible. All other data should be regarded as predictions, for which we assumed complete dissociation (ν_s) so that the two lines (blue closed cycles and red crosses) are identical.

Only in case of EQM water activity measurements we could determine the effective dissociation (ν_e) by using an optimal fit of Eq. (20) to the measurements where necessary, as for instance for NH_4Cl . The accuracy of the results of Eq. (20) is then dependent on the accuracy of these measurements. However, strong electrolytes practically completely dissociate; NaNO_3 and NaCl have almost identical ν_s and ν_e , which provides some confidence in both the measurements and Eq. (20). For cases where ν_s and ν_e differ we can see the sensitivity of Eq. (20) to these parameters. Similarly, the single solute molality estimates based on simple solubility approximations (filled, turquoise squares) additionally indicate the sensitivity of $m_{ss}(\text{RH})$ to uncertainties in the solubility data. It is important to note that only concentration independent constants have been used over the entire concentration range to predict the single solute molalities of various solutes for all cases. ¹

¹The single solute molality measurements in the CRC Handbook are listed as a function of solubility ($W_s=100 \cdot w_s$) rather than water activity (a_w). We therefore plotted the molality (black crosses) against the water activity only in case the solubility values matched those derived from Eq. (20). Although this can lead to a bias in the comparison, in particular for the steepness of the $m_{ss}(\text{RH})$ functions, we can evaluate the accuracy of this comparison for all cases where we additionally have measurements available, as used in EQMs. Since the agreement is rather good, and since the CRC solubility measurements and those derived from Eq. (20) must match at the saturation water activity (i.e. at the RHD), which fixes the steepness of the $m_{ss}(\text{RH})$ function, we have included the CRC measurements also for cases where we do not have independent measurements. Especially the steepness of the $m_{ss}(\text{RH})$ functions of the 7 non-electrolytes (Table 1; for figures see electronic supplement <http://www>.

3.6 Relative humidity of deliquescence (RHD)

The relative humidity of deliquescence (RHD) describes the relative humidity at which a solid salt deliquesces through water uptake. Since a solution is saturated at equilibrium the corresponding RH must equal the RHD of the salt. The RHD can therefore be directly computed from Eq. (20). After rearranging Eq. (20) and solving for RH, i.e. with RH = RHD

$$\text{RHD} = \left(\nu_e / \nu_w m_{SS}^{\nu_e / \nu_w} / 55.51 + 1 \right)^{-1} . \quad (21)$$

Table 2 lists RHD values as used by EQMs (see e.g. Metzger, 2000 for details) and previously applied by Metzger et al. (2002, 2006), and Table 3 lists various RHD values obtained with Eq. (21). Note that Table 2 only contains RHD values for those compounds of Table 1 included in the cited EQMs, while Table 3 lists (predicted) RHD values for all compounds of Table 1. Note further that the RHD values obtained from Eq. (21) provide additional independent support for the accuracy of Eq. (20), and another possibility for evaluation with RHD measurements or independent calculations.

3.7 Aerosol associated water mass

The water mass associated with atmospheric aerosols can be directly obtained for single solute or mixed solutions from the definition of molality ($m_{SS} = n_s / n_w 55.51$) by atmos-chem-phys-discuss.net/7/849/2007/acpd-7-849-2007-supplement.zip strongly depend on the assumptions for ν_e and ν_s . By assuming a value of one for either ν_e or ν_s , the steepness of all $m_{SS}(\text{RH})$ functions of the 7 non-electrolytes increase as strongly as the one of ammonia (NH_3), which seems unrealistic for the alcohols and sugars as it would indicate a very low solubility. Furthermore, the agreement with CRC measurements is then quite poor, as only the very first water activity measurements near unity match (not shown). Only for the ν_e and ν_s values given in Table 1, the relative best agreement with the CRC measurements is achieved in terms of a maximum number of solubility data points that matches. This indicates, however, that – probably as a rule of thumb – approximately each fractional group or oxygen atom becomes hydrated, so that e.g. $\nu_e = 11$ for D- mannitol and sucrose.

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using Eq. (20)

$$m_{w,ss} = n_s/m_{ss} = n_s \cdot [v_w/v_e 55.51 (1/RH - 1)]^{-v_w/v_e} \quad (22)$$

The total water mass associated with a mixed solution containing n -single solutes is – because of the underlying principles of an osmotic system in particular the pressure additivity – the sum of the water masses associated with all single solute solutions

$$m_w = \sum_{j=1}^n n_{s,j}/m_{ss,j} \quad (23)$$

Similarly as Fig. 2a for four selected compounds, Fig. 2b shows that the water mass associated with single solutes is much less sensitive to the uncertainty in solubility as the calculated single solute molalities. This can be seen for the case of equivalent solute masses, where each single solute solution contains 1 μ g of solute plotted as a function of RH (Fig. 2b).

Firstly, in the case where RH approaches unity, the water mass is limited only by the saturation water vapor mass, which is a function of temperature. For all other cases (RH<1), the water mass is limited only by the availability of water vapor. Secondly, different hygroscopicities of salt solutes yield, however, a) a different amount of aerosol associated water for a given RH and b) a different RHD, which determines (i) the RH at which a solution is saturated with respect to a dissolved salt and (ii) the range where water is associated. Less soluble salts have a smaller range where they can take up water, i.e. they follow a higher RHD, which means they precipitate more rapidly from the solution as the water activity deviates more strongly from unity.

Note this is very important for aerosol optical and air pollution aspects. For instance, the deliquescence behavior of natural aerosol compounds, which include e.g. NaCl and MgCl₂, changes considerably through the mixing with air pollution, whereby the chlorides are often replaced by nitrates and sulfates, which have different RHDs (see Table 3). Air pollution can thus drastically alter the RHD of sea salt aerosol particles, reduce the equilibrium radius, and thus modify the scattering properties. Furthermore,

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the water mass associated with a certain amount of solute also depends on the salt component. Lighter salt compounds typically bind a larger mass of water. For instance, 1 μg of ammonium chloride (NH_4Cl) in air pollution would trap approximately the same amount of water as NaCl. According to Fig. 2b, at $\text{RH}=80\%$ both would be associated with approximately 30 μg of water, while NaNO_3 and ammonium nitrate (NH_4NO_3) would fix only about half that amount though over a different range of RH.

4 Equilibrium model

4.1 EQSAM3

The theoretical considerations of the previous sections have been incorporated into the third version of the thermodynamic Equilibrium Simplified Aerosol Model, EQSAM3, building on earlier versions presented by Metzger et al. (2002, 2006). The model computes the gas/liquid/solid partitioning of all compounds listed in Table 1, whereby only the – measured – solubility is required as input for each compound. Previous EQSAM versions additionally used equilibrium constants and tabulated RHD values, and a partitioning in certain chemical domains and sub-domains, similar to other EQMs. EQSAM3 analytically solves the gas/liquid/solid partitioning of almost 100 compounds without further constraints on the aerosol system.

The model set up is as follows:

1. The model is initialized using the thermodynamic data provided in Table 1, whereby the stoichiometric constants for water (v_w) and solute (v_e) can be either prescribed, or v_w can be computed online from Eq. (19) to account for the temperature dependency of the solubility.
2. Since the underlying physical principles are governed by those of an osmotic system, for which the gas-solution analogy is appropriate (see Sect. 2.1.2), we assume that the temperature dependency is described by the gas law, i.e. that

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it is sufficient for most compounds to multiply Eq. (20) by T_o/T . T_o is the temperature at which the solubility listed in Table 1 has been measured (for most compounds $T_o=298.15$ [K]). Note that this describes the temperature dependency of the gas/aerosol system, since the solubility is used to calculate all other thermodynamic properties (v_w , m_{SS} , m_w , RHD).

3. Subsequent to v_w and v_o the single solute molalities are obtained according to Eq. (20) as a function of RH (and T).
4. The water mass of single solute and mixed solutions is computed according to Eqs. (22) and (23). Note that Eq. (23) directly follows from the principles of an osmotic system, i.e. from the additivity of the partial pressures, a consequence of the gas-solution analogy. Note further that Eq. (23) is equivalent to the ZSR-relation, an assumption on the additivity of partial water masses widely used in atmospheric modeling, as empirically established according to Zdanovskii (1948), Stokes and Robinson (1966).
5. For single solute solutions, the relative humidities of deliquescence are calculated from Eq. (21). For mixed solutions, the RHD is calculated from Eq. (21) by using mean values (v_w , m_{SS} , m_w); the latter are computed for mixed salt solutions at a given RH and T.
6. The reaction order can be either prescribed or determined automatically based on the RHD of the solutes. We consider that the reaction order is primarily determined by the solubility. Compounds with a low solubility precipitate from solution already at relatively high RH, so that these ions are not available for further reactions. For instance, the solubility of calcium sulfate (CaSO_4) is very low (<1%) which leads to precipitation of CaSO_4 at a RH close to 100% (Table 2). CaSO_4 and other low-soluble salt compounds are therefore regarded as pure solids over the entire RH range.

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(a) In case the reaction order is prescribed, we rank the ions towards their ability of neutralization, by which we adopt the Hofmeister series (Hofmeister, 1888) to account for the degree to which ions bind to water (salting-out effect) that increases the effective concentration of the ions (in the remaining “free” water) so that they precipitate, thus releasing low entropy surface water (for details, see e.g. <http://www.lsbu.ac.uk/water/> for details).

(b) We assume the following single solute neutralization order, by which the ions to the left become preferentially neutralized:

Anions: $\text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{HSO}_4^- > \text{NO}_3^- > \text{Cl}^- > \text{Br}^- > \text{I}^- > \text{CO}_3^{2-} > \text{HCO}_3^- > \text{OH}^- > \text{CHO}_2^- > \text{C}_2\text{H}_3\text{O}_2^- > \text{C}_2\text{O}_4^{2-} > \text{C}_6\text{H}_5\text{O}_7^{3-}$

Cations: $\text{Fe}^{3+} > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{Na}^+ > \text{K}^+ > \text{NH}_4^+ > \text{H}^+$

Note that this neutralization order is preliminary and requires additional measurements.

7. Based on the reaction order (prescribed or automatically determined for given T, RH) the solute compounds and the non-neutralized “free” ions are computed. The H^+ concentration is explicitly calculated starting from electroneutrality of the solution, by accounting for the auto-dissociation of water and optionally on the effect of atmospheric CO_2 on the pH. At this point all compounds are considered in the aqueous phase. Then the RHD of all single solute and of the mixed solution is calculated, and subsequently the liquid/solid partitioning, whereby all compounds for which the RHD is below that of the mixed solution are assumed to be precipitated (solid).

8. Gas/liquid partitioning is calculated for all (semi-)volatile gases, i.e. all hydrogen compounds (first row of Table 1) except phosphoric and sulfuric acid, which are treated as non-volatile due their very low vapor pressure.

9. For (semi-)volatile compounds activity coefficients are used. For other compounds they are not needed. Non-volatile compounds remain in the aqueous

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or solid phase independent of the solute concentration, and the liquid/solid partitioning is merely determined by the solute solubility. Since the water mass is proportional only to the solute mass (at a given T, RH) activity coefficients are not needed. For (semi-)volatile compounds activity coefficients are computed from Eqs. (14), (20), whereby we account for what we call the molal charge density of the solute (Metzger et al., 2000, 2002). Mean molal binary activity coefficients of volatile compounds are thus obtained from

$\gamma_{S,j} = \left(\text{RH}^{-\nu_w/\nu_e} / [\nu_w/\nu_e 55.51 (1/\text{RH} - 1)]^{\nu_w/\nu_e} \right)^{2/\xi_{S,j}}$; activity coefficients of the corresponding cations (γ_{S+}) and anions (γ_{S-}) can be computed from Eq. (16), as-

suming $\gamma_{S+}^{\nu_e^+} = \gamma_{S-}^{\nu_e^-}$ in accord with Eq. (15). $\xi_{S,j}$ expresses the effective ion charge of the hydrated/dissociated solute relative to the charge of the water ions involved in the hydration (which act as a dielectricum reducing the electrical forces of the solute cation and anions). $\xi_{S,j} = N_{\pm} \nu_e / Z_{S,j}^{\pm}$ with $Z_{S,j}^{\pm} = Z_{S+,j}^{\nu_e^+} + Z_{S-,j}^{\nu_e^-}$ the total charge of the ion-pair of the j th-compound with $N_{\pm} = k_{\pm}^{K_{\pm}}$ and $k_{\pm} = 2$ accounting for the fact that 2 moles of water are consumed for each mole of H_3O^+ produced (assuming electroneutrality for dissociation reactions). For instance, for the volatile ammonium salts NH_4NO_3 and NH_4Cl $Z_{S,j}^{\pm} = 1^{\nu_e^+} + 1^{\nu_e^-} = 2$, ν_e , is given in Table 1 and $N_{\pm} = 4$.

10. The residual gases and acids (all hydrogen compounds, first row of Table 1) are computed from the remaining cations and anions, whereby (semi-)volatile acids are assumed to remain in the gas phase if not neutralized, or taken up directly from the aqueous solution (which however yields only small amounts relative to the total particulate matter).

11. Non-electrolyte solutes (last row of Table 1) are, except ammonia (NH_3), not directly considered for the determination of the reaction order, nor are they assumed to be involved in neutralization reactions. However, they contribute to the aerosol

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mass, and as long as they remain in the aqueous phase to the aerosol water mass.

12. Various aerosol properties can be computed and stored for diagnosis, including aerosol properties difficult to measure, such as the $pH = -\log \sum_{j=1}^{l(aq)} (n_{s,+j}/m_w)$, or

5 the ionic strength of the solution $Z = 0.5 \cdot (Z_{s,+} + Z_{s,-}) / m_w$, with $Z_{s,+} = \sum_{j=1}^{l(aq)} z_{s,+j}^{v_e^+}$ and

$Z_{s,-} = \sum_{j=1}^{l(aq)} z_{s,-j}^{v_e^-}$ the total charge of the cations and anions, respectively. Aerosol

properties such as mass or number of moles of each compound and associated water can be stored for each compound (yielding listings similar to Table 3). Additionally, the total particulate matter (PM), including solids and ions,

10 can be expressed as the total number of moles, $PM = \sum_{j=1}^{l(aq)} n_{s(aq),j} + \sum_{j=1}^{l(cr)} n_{s(cr),j}$, al-

ternatively as total mass, $PMt = \sum_{j=1}^{l(aq)} n_{s(aq),j} M_{s,j} + \sum_{j=1}^{l(cr)} n_{s(cr),j} M_{s,j}$, or total dry mass

$PMs = \sum_{j=1}^{l(cr)} n_{s(cr),j} M_{s,j}$, whereby the mass fractions of all individual compounds are

explicitly summarized upon their molar masses $M_{s,j}$, as is the total aerosol associated water mass following Eq. (23).

15 Note that the model structure of EQSAM2 (Metzger et al., 2006) has been adopted also in EQSAM3, however, EQSAM2 was not based on solubilities. Instead it used equilibrium constants and prescribed deliquescence relative humidities as listed in Metzger (2000), and activity coefficients for volatile compounds according to Metzger et al. (2002). The underlying physical principles are nevertheless the same. An example application of EQSAM2 and EQSAM3 is given in the next section. Both model versions

are available for the scientific community upon request.

4.2 Comparison with measurements

Here we apply EQSAM3 to the MINOS (Mediterranean INTensive Oxidant Study) measurements on Crete in the period 27 July to 25 August 2001, by extending the model-data comparison of Metzger et al. (2006). For a general description of the measurements and the model comparison set-up we refer to that article. We focus on the application of EQSAM3 to mixed solutions and a comparison with other EQMs (EQSAM2, ISORROPIA, SCAPE2) by applying all models at the same level of complexity. Note we focus on the chemical system F2/C2 defined in Metzger et al. (2006), i.e. the ammonium/sulfate/nitrate/chloride/sodium/water system.

Figure 3 shows 4-weekly time series of various model calculated mixed solution properties; observations are included where available. Figure 3a shows that the total fine and coarse mode aerosol associated water mass is consistently predicted by the EQMs, assuming metastable aerosols (gas/liquid partitioning) with EQSAM3, EQSAM2 and ISORROPIA. Particularly the results of EQSAM3 and ISORROPIA are relatively close; SCAPE2 deviates most significantly for the dry periods because the assumption of metastable aerosols breaks down. Instead, SCAPE2 calculates the full gas/liquid/solid partitioning. These results (in particular the deviations) provide a rough indication of the relative importance of the deliquescence thresholds (RHD values), important for the partitioning between the solid and aqueous phase.

All model predictions of the total number of particulate matter (PM) moles, including solids and aqueous phase compounds, are in good agreement for both the fine and coarse mode. EQSAM2 shows relatively largest deviations for the fine mode. The results of EQSAM3 appear to be closest to ISORROPIA, which might be conceived as a reference model associated with its high degree of numerical accuracy (and computational costs).

Focusing further on the fine mode, Fig. 3b shows that all models consistently predict the total PM and, because all models account for the full gas/liquid/solid partitioning,

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also the associated dry aerosol mass fraction. Again, the relatively largest deviations can be attributed to differences in the RHD calculations; except SCAPE2 all models account for the RHD of mixed solutions, whereby EQSAM2 uses a combination of RHD values from both ISORROPIA and SCAPE2, i.e. mutual deliquescence RHDs of ISORROPIA when available, and RHDs of SCAPE2 for all mineral salt compounds (which are not considered in ISORROPIA). EQSAM3 consistently computes all RHDs (of single solute or mixed solutions) from Eq. (21), whereby mean values are used for mixed solutions as described above. Figure 3b furthermore shows that even the predictions of very sensitive aerosol properties such as the mean binary activity coefficients (shown is the one of ammonium nitrate in the mixed solution) and the solution pH are in general agreement.

Figure 3c demonstrates that all EQMs predict the residual gaseous ammonia and nitric acid and the corresponding aerosol ammonium and nitrate. Especially the calculations of the lowest measured aerosol nitrate concentrations are most accurate with EQSAM3, being quite sensitive to the activity coefficient of ammonium nitrate. Note that the models do not necessarily need to be in agreement with all observations for ammonia/ammonium. The reason is that mineral cations and organic acids are omitted in the EQM comparison because ISORROPIA does not account for these compounds. Metzger et al. (2006) showed that the presence of ammonium in the aerosol phase is dependent on the presence of organic acids (e.g. from biomass burning) in cases where alkali-cations (e.g. mineral dust) are present in excess of inorganic acids. In fact, the consistent inclusion of alkali-cations and organic acids is important for the gas/aerosol partitioning of reactive nitrogen compounds for both fine and coarse mode particles. In contrast to ammonium, nitrate in the fine mode is less affected than in the coarse mode, so that the aerosol nitrate predictions of EQSAM3, which are closest to the observations for this sensitive case, also give evidence for its applicability.

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4.3 Application outlook

To indicate the potential of our theoretical considerations and implications for atmospheric pollution and climate modeling, we present in this section a preview of some applications in progress with EQSAM3, including visibility predictions and aerosol/cloud interactions. For details we refer to future publications.

4.3.1 Visibility predictions

Under humid conditions, hygroscopic aerosol particles can substantially reduce atmospheric visibility. Figure 4 presents four different visibility predictions with EQSAM3, compared with observations at the Meteorological Observatory Hohenpeißenberg (MOHp), Germany, for October 2003. The “translation” of PM concentration and particle size into visibility, based on aerosol optical parameters, will be described elsewhere. The four panels differ only in assumptions about the aerosol composition and size, all computed analytically with EQSAM3. We focus on the relative differences because they provide indications of the sensitivity of the results to these assumptions.

Assuming the total observed PM to consist of pure ammonium sulfate (AS) with particle radii of 60 nm leads to a lower visibility than observed, whereas micrometer sized particles of the same composition yield a much too high visibility (left two panels of Fig. 4). Visibility calculations based on 120 nm sized AS particles predict conditions of low visibility rather well, while the same size particles composed of 50% ammonium sulfate and 50% of low molecular weight (LMW) organic acids (e.g. formic and acetic acid) produce the best results, in particular also for high visibility. Remarkably, even in cases where precipitation was observed the model based on 120 nm sizes AS particles predicts the low visibility rather well. This provides a first indication that there exists overlap between conditions of high aerosol associated water and cloud formation.

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4.3.2 Global applications

Our preliminary global modeling applications focus on the role of the aerosol water mass, being highly relevant for climate forcing estimates. Note that present climate models that include aerosols do not explicitly calculate aerosol water. Here we aim to show that EQSAM3 can provide a computationally efficient alternative that does not only accurately simulates the aerosol chemical composition but also the most abundant aerosol species: water.

We apply the general circulation model ECHAM5 (Roeckner et al., 2003) at T63 (~ 1.9 degree), resolution, extended with the comprehensive Modular Earth Submodel System (MESSy) to account for atmospheric chemistry (Jöckel et al., 2006). The model will be abbreviated in the following as E5M1. It has been additionally extended by the MESSy version of EQSAM (<http://www.messy-interface.org/>), which accounts for 7 aerosol modes, including four soluble and three insoluble: nucleation, aiten, accumulation and coarse, by which the latter three modes are used to distinguish between primary insoluble and soluble aerosol species such as black carbon or certain mineral dust compounds (similar as in Vignati et al., 2004). Details will be provided in a follow-up publication.

Various aerosol species

Figure 5a presents a “snapshot” of the model results for 9 September 2000 (12:00 GMT) by showing the spatial distribution (vertical integral) of various fine mode aerosol species, including aerosol associated water mass [$\mu\text{g}/\text{m}^2$], aerosol nitrate, ammonium, sulfate, organic carbon, and sea salt [parts per billion by volume, ppb] (from top left to bottom right). While certain aerosol species such as nitrates and organics are largely confined to continental areas, associated with the localized emission sources, other species such as ammonium and sulfate show much wider dispersion. Fine mode ammonium is highly correlated with sulfate, and can be transported over long distances. Nitrate compounds are volatile and they are also found on coarse mode

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particles, such as sea salt and mineral dust, which are more efficiently deposited.

Figure 5a also shows that the spatial distribution of aerosol associated water (RH<0.95) strongly correlates with that of sea salt, sulfate and ammonium, and that at this arbitrary RH limit the aerosol associated water mass already dominates the total aerosol load. Figure 5b shows the tropospheric aerosol associated water mass, while Fig. 5c presents the corresponding aerosol water in the upper troposphere - lower stratosphere (UTLS) region. These figures are complementary and illustrate the dependence on synoptic weather conditions.

Cloud cover

In a case for which we do not limit the RH to 95%, as in the previous example, aerosol water strongly increases when RH approaches unity. This directly follows from the thermodynamic principles described in Sect. 2 and can be best seen from Eq. (5). Note that the aerosol water mass calculated from Eq. (23) involves Eq. (20), based on Eq. (5). Applying Eq. (5) to atmospheric conditions requires, however, that the condensation of water vapor is limited by the availability of water vapor which is determined by RH and the saturation water vapor. Thus we use the following thermodynamic constraints to limit the condensation of water vapor, and hence the aerosol associated water mass for atmospheric applications:

1. Limit the condensing amount of water by the availability of water vapor; this encompasses all conditions with $RH < 1$.
2. Limit the condensing amount of water by the amount of water vapor constrained by the saturation water vapor, being a function of temperature; encompassing cases with $RH \geq 1$.
3. Correct the water vapor concentration for the condensed amount of water vapor (aerosol associated water mass), which becomes important for all cases where

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RH approaches unity, in particular for the UTLS region, but also for all regions where aerosol water overlaps with cloud water/ice presence.

Subsequently, we directly compute the cloud cover from the total aerosol load (including water) by assuming total coverage of the relevant model grid cells (i.e. a cloud cover fraction of unity) in case the aerosol load exceeds an amount that is determined by the saturation water vapor mass at a given temperature. The cloud cover therefore depends on:

1. the amount of total particulate aerosol matter (PM_t); according to Eq. (23) the aerosol associated water mass is proportional to PM_t (illustrated in Fig. 2b)
2. the type of PM_t; according to Eq. (20) the aerosol associated water mass depends on the type of solute (illustrated in Figs. 2a, b)
3. the temperature, which determines the saturation water vapor and hence the maximum amount of water available for condensation leading to hygroscopic growth of aerosols; hazy conditions are favored by high aerosol load (dominated by hygroscopic salt solutes) and low temperatures. When the ambient temperature drops below the dew point temperature, the water vapor concentration exceeds the amount of water vapor that can be taken up by the air so that it is saturated with respect to water vapor; additional water vapor directly condenses, which leads to fogs, hazes and clouds.

Figure 5d shows the cloud cover corresponding to Figs. 5a–c, diagnosed from the total aerosol load as described above (without aerosol-cloud and radiation feedbacks), which shows similar synoptic patterns as the aerosol associated water shown earlier. Figure 5e further depicts a regional focus, which qualitatively compares calculations with and without EQSAM3 to satellite observations. The lower panel shows the cloud cover as observed from space (GEOS channel 4), while the upper left panel shows the cloud cover prediction of the base E5M1 model; in the upper right panel the cloud

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cover is based on the EQSAM3 water uptake calculations. The latter seem to compare better with the satellite observations, indicating that especially optically thin clouds are better resolved if aerosol associated water is accounted for. This issue deserves more attention, including additional model tests and optimization, and will be considered in a future work.

Cloud ice

Figures 5c and e indicate that especially optically thin clouds may be described by aerosol associated water model predictions. If aerosols are treated comprehensively, as described above, there is actually no principal physical difference between aerosol associated water, cloud water and cloud ice, and the subdivision is to some degree arbitrary as determined by the droplet size.

To investigate to what extent the cloud ice content can be directly calculated, Fig. 6 presents an additional snap shot for 3 June 2004 (12:00 GMT), comparing the base model (left two panels) with that including EQSAM3 for the troposphere (top panels) and the UTLS region (bottom panels). The calculations including EQSAM3 assume that the excess aerosol water with respect to the limit based on the saturation water mass represents the condensed cloud water mass. In addition, the freezing point depression associated with salt solutes was taken into account and computed from the total number of solute moles in solution and the cryoscopic constant of water, which is $1.86 \text{ [K mol}^{-1}\text{]}$.

Figure 6 (middle panels) shows that the ice content and distribution predicted by EQSAM3 compares qualitatively, though remarkably well with the original E5M1 parameterized ice clouds, in particularly for the UTLS region. Contrasting the explicit treatment of freezing point depression with a simpler constraint, i.e. fixing the freezing point temperature to a constant $T=243 \text{ [K]}$, both with the same aerosol load, shows poorer agreement, being most noticeable for the UTLS. This comparison – though not rigorous – indicates that:

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1. the explicit prediction of aerosol associated water mass enables the direct calculation of large scale (i.e. model grid scale) cloud properties, and
2. cloud properties are sensitive to aerosol chemistry; the latter determines the particle hygroscopic growth, which in turn controls the size distributions of aerosols and the cloud at its initial formation.

To consistently apply these concepts in regional and global cloud modeling studies it will be necessary to fully couple EQSAM3 with other cloud processes such as the collision and coalescence of droplets and precipitation formation.

5 Summary and discussion

5.1 From laboratory to atmosphere

Under controlled laboratory conditions, the water mass is fixed so that solution properties such as the solute molarity or molality can be measured, upon which non-ideal solution properties such as activity coefficients can be defined. Application to the atmosphere requires the transformation of these solution properties with respect to water, i.e. the water mass needs to be a function of relative humidity.

In the atmosphere aerosol and cloud water depend both on the water vapor mass. In turn, the water vapor mass is to a large extent controlled by the ambient temperature (T), which determines both the amount of water vapor available through evaporation and the maximum amount of water vapor that the air can contain at a given T . The ratio of the actual water vapor concentration to the maximum concentration at saturation (at the same T) is the relative humidity (RH). At $RH \geq 1$ the air is saturated with respect to water vapor, and excess water vapor condenses to the aqueous or ice phase, while at $RH < 1$ the air is subsaturated, so that only a fraction of the saturation water mass is in equilibrium with the aqueous phase.

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The maximum amount of aerosol water at subsaturation is limited only by the available water vapor mass, and at saturation or supersaturation by the T -dependent maximum water vapor mass. Under all conditions, at thermodynamic equilibrium the condensed water mass is proportional to the mass of the solute, since the RH determines the water activity of the solution.

5.2 Conceptual difficulty

The water activity of atmospheric aerosols thus depends on both the amount of solute in solution and the associated amount of water, whereby aerosol water is a function of RH. Previously, however, equilibrium aerosol thermodynamics (see e.g. Wexler and Potukuchi, 1998 for a review) did not account for the amount of water involved in the dissociation of e.g. salt solutes. Water was only considered when explicitly consumed or produced. We alleviate this limitation by reformulating aerosol and cloud thermodynamics to consistently account for the water associated with the hydration of solutes. The underlying physical principles that govern hydration have been adopted and generalized from osmosis.

5.3 Osmosis

Following Arrhenius' theory of partial dissociation and the original description of osmosis by van't Hoff and Ostwald, we extend van't Hoff's gas-solution analogy to non-ideal solutions by introducing a stoichiometric coefficient for water ($\nu_w = \nu_w^+ + \nu_w^-$) to account for the actual number of moles of water causing hydration. An associated effective coefficient for the solute ($\nu_e = \nu_e^+ + \nu_e^-$) accounts for the effective number of moles arising from partial or complete solute dissociation. The advantage of these stoichiometric coefficients is that they can be assumed constant over the entire solute activity range. For a further discussion about the state of dissociation of electrolytes in solutions we refer the interested reader to Heyrovská (1989).

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5.4 Solubility

Common with Heyrovska (1989), we use solute specific coefficients to calculate the vapor pressure reduction over a wide concentration range. In contrast to Heyrovska (1989), who did not perform the transformation to atmospheric conditions, we use the transformation invariant coefficients ν_w and ν_e , whereby we derive ν_w from the solute solubility according to Eq. (19). The advantage is that only one – easily measured and commonly used – solubility value is needed. The disadvantage is that for salt solutes that do not dissociate completely the effective dissociation constant ν_e must be known. However, ν_e can be determined from ν_w by Eq. (20) if compared to water activity measurements.

5.5 Water activity

Although the discussion of water activity is intricate, being relevant to many areas including for instance the pharmaceutical and food industries (see e.g. the web portal by M. Chaplin <http://www.lsbu.ac.uk/water/activity.html>), atmospheric applications allow for some simplifications, as shown in this work. One reason is that at equilibrium the osmotic pressure expressed in terms of water, e.g. associated with the hydration of a salt solute, equals the partial vapor pressure of water, so that the water activity remains constant and equal to RH (Sect. 2). One important consequence is that the amount of water required for hydration is directly proportional to the amount of solute.

5.6 Kelvin-term

Another consequence, not addressed thus far, is that the vapor pressure reduction associated with dissolution, hydration and dissociation of a solute equals the osmotic pressure difference, independently of the curvature of the surface (see Fig. 1). At equilibrium the osmotic pressure of the solute or solvent (in solution) equals the corresponding partial vapor pressures of solute or solvent above the solution. In contrast

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to the theoretical solvent partial pressure in solution, the (measurable) osmotic pressure is an effective pressure and hence implicitly accounts for any surface tension or non-ideality effects. Note that Raoult's law describes this for the solvent and Henry's law for the solute, and both can be generalized to account for solution non-idealities by including either activity coefficients or the stoichiometric coefficients ν_w and ν_e .

The use of the latter has the advantage that the water uptake of atmospheric aerosols can directly be calculated from the osmotic pressure (difference). Hence at equilibrium the so called "Kelvin-term" that accounts for the curvature of nanometer sized particles is not needed. However, such small particles are rarely in equilibrium with the ambient air; rather they grow relatively fast due to hygroscopic growth, whereby their equilibrium size is maintained by RH. Thus, except for the calculation of nucleation grow rates (non-equilibrium conditions) surface curvature corrections are not required.

5.7 Köhler-equation

Another consequence is that the widely used Köhler-equation becomes redundant, since the Kelvin-term is not required for the calculation of the equilibrium size of the aerosol particles if aerosol associated water is consistently accounted for. In fact, the use of the Köhler-equation is somewhat misleading, since most approximations of the $1/r - 1/r^3$ - radius dependency of the "surface-(Kelvin)" and "volume (Raoult)" term in the Köhler equation are inaccurate. Usually, neither concentration changes in the surface tension are accounted for nor is the fact that the volume of water is not constant but dependent on relative humidity.

By explicitly including aerosol associated water the $1/r - 1/r^3$ radius dependency is automatically accounted for. Note that r is usually approximated as the ambient radius (e.g. Pruppacher and Klett, 1997), while the more explicit formulation (see e.g. Dufour and Defay, 1963) actually yields a difference between the ambient (wet) radius and the dry radius of the solute, expressing the radius of the aerosol associated water which, however, cancels out if the volume occupied by water is not assumed to be constant.

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5.8 Cloud condensation nuclei

Nevertheless, the Köhler-equation has been successfully used in many applications to calculate the activation of aerosol particles as cloud condensation nuclei (CCN) and describe cloud droplet size spectra. Is this really needed, since the definition of CCN requires that a specific though arbitrary supersaturation is prescribed? As illustrated in Sect. 4.3, aerosol particles can grow by water uptake into cloud droplets simply by allowing ambient conditions to include $RH \geq 1$. Obviously, the growing particles compete for the available water vapor, and the likelihood for larger droplets to collect the available water vapor is highest, so that they grow at the expense of smaller ones. Hence, at equilibrium a bimodal size distribution establishes with larger droplets and smaller ones that have collected more and less water vapor, respectively. The larger ones can settle gravitationally dependent on their mass and local vertical air velocities, and by collision and coalescence they can ultimately grow into rain drops. The equilibrium droplet size distribution to a large extent depends on the cloud dynamics, whereas the initial size is determined by the aerosol water mass. Therefore, our method eliminates the need to define CCN. It furthermore allows to directly relate the chemical properties of aerosol particles to cloud droplets, being a requirement to explicitly link emission sources of atmospheric trace constituents in models to the physical properties of aerosol particles, haze and clouds.

5.9 Final comments

Our new concept developed in Sect. 2 uses the fundamental equations and ideas proposed more than a century ago to explain the principles of osmosis. Our contribution is that we have applied and transformed these ideas by consistently accounting for water involved in the hydration of salt or non-electrolyte solutes by the introduction of the stoichiometric constants ν_w and ν_e . This yields both a) a more general formulation of the principles that govern osmosis that now extends to non-ideal solutions, and b) a consistent calculation of the hygroscopic growth of atmospheric aerosols.

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5.9.1 Mixed solutions

It is worth mentioning that the use of ν_w, ν_e is not only limited to the calculation of single solute solution molalities or dilute solutions. As demonstrated by the application of EQSAM3 to observations of sea salt, desert dust and pollution particles over the Mediterranean Sea, ν_w, ν_e can also be assumed constant for highly concentrated mixed solutions (see Fig. 3).

5.9.2 Gibbs free energy

The consistent use of ν_w, ν_e also eliminates the need to iteratively minimize the Gibbs free energy in model applications, since at equilibrium the total Gibbs free energy change must be zero when water is included in the summation. As a consequence, the gas/liquid/solid partitioning can be solved analytically, which saves a considerable amount of CPU-time (see also Metzger et al., 2002) so that applications in complex regional or global models become feasible.

5.9.3 Equilibrium constants

The consistent use of ν_w, ν_e furthermore substitutes the use of equilibrium constants, since the Gibbs free energy is zero and ν_w implicitly includes the relevant information to compute the equilibrium phase partitioning as it is derived from the solute solubility. The successful application of EQSAM3 demonstrates that this approach suffices (Fig. 3). Note that EQSAM3 merely uses solubilities as measured for each solute in Table 1.

5.9.4 Relative humidity of deliquescence

The use of solubility measurements together with ν_w, ν_e yields the relative humidity of deliquescence (RHD), which corresponds to the RH at which the solution is saturated with respect to a solute. Any increase of the solute then results in its precipitation, whereby the solid is in equilibrium with its ions in the aqueous phase. If Eq. (21)

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is used, complex computations are redundant. Even supersaturated conditions may be accessible if the required solubility data are available. Note that the RHD computed from Eq. (21) provides independent evidence of the accuracy of Eq. (20) and the applicability of v_w, v_e to concentrated mixed solutions. Previous approaches were dependent on activity coefficients.

5.9.5 Activity coefficients

With the successful application of EQSAM3 we further demonstrate that activity coefficient are not required when v_w, v_e are used to calculate the aerosol associated water mass, because RH determines the water activity (note that $RH < 1$ is already a correction for solution non-ideality). Only for (semi-)volatile compounds activity coefficients are needed, as they can be driven out of the aqueous phase into either the precipitating solid or the gas phase when the water activity decreases (i.e. when RH drops). Non-volatile compounds can only be driven out of the aqueous into the solid phase. For saturated solutions this is determined by the solute solubility (at equilibrium a solution is always saturated). Substituting Eq. (20) into Eq. (14), and considering Eqs. (15) and (16), activity coefficients can be directly computed from RH when v_w, v_e are known (Sect. 4.1). For instance, the calculated mean binary molal-activity coefficient of ammonium nitrate compares well with that computed independently by ISORROPIA, also for concentrated mixed solutions (Fig. 3). Even very sensitive aerosol properties such as the solution pH compare well, and low aerosol nitrate concentrations can be effectively predicted. Although very low aerosol nitrate concentrations could not be predicted with EQSAM2 (mainly since the use of the ammonium nitrate equilibrium constant is insufficient for certain mixed aerosol systems) the mean binary activity coefficient of ammonium nitrate is comparable in both versions. Note that EQSAM2 used activity coefficients that have been derived according to the method described in Metzger et al. (2002). Zaveri et al. (2005) compared this method with various other and well established activity coefficient calculation methods and recognized that this was the first time to express binary mean activity coefficients of individual electrolytes directly as

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a function of water activity. Unfortunately, Zaveri et al. (2005) have overlooked that the method of Metzger et al. (2002) is not limited to dilute binary systems but also extends to multicomponent activity coefficients of concentrated mixed solutions, as demonstrated in Fig. 3. The reason is that Zaveri et al. (2005) applied these methods to laboratory conditions without the required transformation to the atmosphere, a conceptual difficulty we hope to have eliminated with our present work.

5.9.6 Equilibrium assumption

The equilibrium assumption is an essential and central element in physical chemistry. For instance, Henry's Law constant describes the partitioning of a gas between the atmosphere and the aqueous phase. It can be based on direct measurements or calculated as the ratio of the pure compound vapor pressure to the solubility. The latter approximation is reliable only for compounds of very low solubility. In fact, values of Henry's law constant found in the literature frequently differ substantially. Despite that Henry's law constants are determined on the basis of equilibrium, they are used to solve chemical systems which are not in equilibrium. Similarly, our formulas can be applied to non-equilibrium conditions by solving the chemical system dynamically. The accuracy achievable with our equations, e.g. Eqs. (20), (21) or (23), merely depends on the accuracy and applicability of the solubility measurements from which the solute specific constants ν_w , ν_e have been derived. Note that this also includes the temperature dependency. The approximation used in EQSAM3 might not necessarily suffice for all compounds, and explicit temperature dependencies can be easily invoked to derive the solute specific constants ν_w and ν_e . The assumption that droplet growth on aerosol particles can be approximated by an equilibrium approach can be conceptually tested by observing the steady state conditions of e.g. stratocumulus and cumulus clouds. Even though droplets continually grow and evaporate by local moisture variations, the cloud appearance (i.e. the mean cloud properties) varies little unless the overall dynamical or thermodynamical boundary conditions change.

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5.9.7 Importance of aerosol associated water

The applicability of ν_w, ν_e to mixed solutions, as determined from single solubility measurements, is particularly useful for atmospheric applications, since complete knowledge of the actual solute composition is often not available. Especially deliquescence relative humidities, which can be calculated from ν_w, ν_e by Eq. (21), are crucial as they determine at which RH the aerosol particles grow into the size range of efficient solar radiation scattering and subsequently of cloud formation.

6 Conclusions

Based on basic thermodynamics principles we explained how water conceptually links osmotic pressure, aerosols, fogs, hazes and clouds. When transformed from laboratory to atmospheric conditions, as summarized by Eqs. (7)–(10), it follows that the water needed for hydration is proportional to the amount of solute and governed by the type of solute and RH. To account for the moles of water needed for hydration and dissociation we introduced the solute specific effective dissociation coefficient ν_e and the coefficient for water, ν_w , both independent of the solute concentration, and they can be directly computed from the solute solubility of electrolytes (salt solutes) or non-electrolytes (e.g. sugars, alcohols, or dissolved gases).

We demonstrated the applicability of this concept in a thermodynamic equilibrium model (EQSAM3) for mixed solutions. The results of EQSAM3 compare well to field measurements and other thermodynamic equilibrium models such as ISORROPIA and SCAPE2. The latter two models use comprehensive (and CPU demanding) algorithms to solve the classical aerosol thermodynamics (being rather complex for mixed solutions), whereas EQSAM3 solves the gas/liquid/solid partitioning and hygroscopic growth analytically and non-iteratively. EQSAM3 computes various aerosol properties that are difficult to measure such as size-segregated particle composition, deliquescence of single or mixed solutions, solution pH, and can account for inorganic and

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organic salt compounds (Table 1 lists nearly 100).

We further illustrated that the water uptake of aerosols is directly proportional to the aerosol load whereby the hygroscopic growth depends on the type of solute. We presented calculations of water uptake as a function of RH for a simple inorganic mixed salt aerosol, which can easily be extended to the nearly 100 compounds in Table 1. It appears that the application of EQSAM3 to visibility predictions is quite promising.

Our outlook for future applications of EQSAM3 also involved global chemistry-transport and meteorological modeling, including aerosol-cloud interactions. The EQSAM3 computation of aerosol associated water – without assumptions about the activation of aerosol particles – holds promise for the explicit computation of large scale hazes and clouds, including cloud cover, the initial cloud water and cloud ice. When aerosol water is explicitly accounted for, aerosol and cloud thermodynamics can be substantially simplified. This approach will allow model calculations that directly relate emissions of natural and anthropogenic trace substances to haze and cloud properties.

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Table 1. (a) Thermodynamic data.

Anions→ Cations↓	Phosphate PO_4^{3-}			Sulfate SO_4^{2-}			Hydrogen Sulfate HSO_4^-			Nitrate NO_3^-			Chloride Cl^-			Bromide Br^-			Iodide I^-		
Hydrogen H^+	H_3PO_4			H_2SO_4			—			HNO_3			HCl			HBr			HI		
	97.995	84.57 ^a	-	98.08	70	1.83	-	-	-	63.01	25	1.513	36.46	15	1.49	80.91	25	3.307	127.9	30	5.228
Ammonium NH_4^+	$(NH_4)_3PO_4 \cdot 3H_2O$			$(NH_4)_2SO_4$			NH_4HSO_4			NH_4NO_3			NH_4Cl			NH_4Br			NH_4I		
	203.1	20	-	132.14	43.31	1.77	115.11	76	1.78	80.04	68.05	1.72	53.49	28.34	1.519	97.94	43.92	2.429	144.9	64.03	2.514
Sodium Na^+	$Na_3PO_4 \cdot 12H_2O$			Na_2SO_4			$NaHSO_4$			$NaNO_3$			$NaCl$			$NaBr$			NaI		
	380.12	12.59	1.62	142.04	21.94	2.7	120.1	22.18	2.43	85	47.7	2.26	58.44	26.47	2.17	102.9	48.61	3.2	149.9	64.79	3.67
Potassium K^+	K_3PO_4			K_2SO_4			$KHSO_4$			KNO_3			KCl			KBr			KI		
	212.3	51.46	2.564	174.3	10.71	2.66	136.2	33.6	2.32	101.1	27.69	2.11	74.55	26.23	1.988	119	40.41	2.74	166	59.68	3.12
Calcium Ca^{2+}	$Ca_3(PO_4)_2$			$CaSO_4$			—			$Ca(NO_3)_2$			$CaCl_2$			$CaBr_2$			CaI_2		
	310.2	.0001 ^a	3.14	136.1	0.205	2.96	-	-	-	164.1	59.02	2.5	111	44.84	2.15	199.9	60.94	3.38	293.9	68.25	3.96
Magnesium Mg^{2+}	$Mg_3(PO_4)_2 \cdot 5H_2O$			$MgSO_4$			—			$Mg(NO_3)_2$			$MgCl_2$			$MgBr_2$			MgI_2		
	352.9	.0001 ^a	-	120.4	26.31	2.66	-	-	-	148.3	41.59	2.3	95.21	35.9	2.325	184.1	50.5	3.72	278.1	59.35	4.43
Iron(II,III) Fe^{2+}, Fe^{3+}	$FePO_4 \cdot 2H_2O$			$Fe_2(SO_4)_3$			—			$Fe(NO_3)_3$			$FeCl_3$			$FeBr_3$			FeI_2		
	186.9	-	2.87	399.9	81.48 ^a	3.1	-	-	-	241.9	45.21 ^a	-	162.2	47.7	2.9	295.6	81.98	4.5	309.7	-	-

Formula

 M_s = Solute molar mass [g/mol] W_s = Solute solubility mass percent [%] ρ_s = Solute density [g/cm³]

M_s	W_s	ρ_s
v_s	v_e	v_w

 v_s = Solute stoichiometric constant, complete dissociation [-] v_e = Solute stoichiometric constant, effective dissociation [-] v_w = Solvent stoichiometric constant, effective dissociation [-] M_s, W_s, ρ_s data from CRC-Handbook of Chemistry and Physics, 85th Edition, 2004–2005.Note. Solubility measurements (W_s) correspond to aqueous solutions at $T=25^\circ C$ except noted: ^a = $15^\circ C$, ^b = $20^\circ C$. M_s, W_s account for the dry mass excluding any mass of hydration. Solvent (water) molar mass $M_w = 18.015$ [g/mol], density of the solution ρ [g/mL].For a compound with low solubility ($W_s < 1\%$) the error from approximating the density is generally less than the uncertainty in the experimental solubility measurement.Relation of $W_s = 100 w_s$ between other common measures of solubility:Solute mass fraction [-]: $w_s = m_s / (m_w + m_s)$ Mass of solute per liter of solution [g/L H₂O]: $R_s = 1000 \rho w_s$ Mass of solute per 100g of H₂O [g/100gH₂O]: $r_s = 100 / (1/w_s - 1)$ Molarity [mol/L]: $C_s = 1000 \rho w_s / M_s$ Molality [mol/kg]: $c_s = 1000 / M_s / (1/w_s - 1)$ Mole fraction [-]: $x_s = (w_s / M_s) / [(w_s / M_s) + (1 - w_s) / M_w]$ Reformulating
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Table 1. (b) Continued.

Anions→ Cations↓	Carbonate CO_3^{2-}			Hydrogen Carbonate HCO_3^-			Hydroxide OH^-			Formate CHO_2^-			Acetate $C_2H_3O_2^-$			Oxalate $C_2O_4^{2-}$			Citrate $C_6H_5O_7^{3-}$		
	H_2CO_3			---			H_2O			CH_2O_2			$C_2H_4O_2$			$C_2H_2O_4$			$C_6H_8O_7$		
Hydrogen H^+	62.025	-	-	-	-	-	18015	100	0.997	46.03	68	1.22	60.05	23	1.045	90.04	8.69'	1.9	192.1	59'	1.665
	3	-	-	-	-	-	2	2	2	2	2	1.833	2	2	1.362	3	3	1.000	4	4	1.470
Ammonium NH_4^+	$(NH_4)_2CO_3$			NH_4HCO_3			NH_4OH			NH_4CHO_2			$NH_4C_2H_3O_2$			$(NH_4)_2C_2O_4$			$(NH_4)_2HC_6H_5O_7$		
	96.086	50.00*	-	79.06	19.87	1.586	35.05	100	-	63.06	58.85	1.27	77.08	59.68	1.073	124.1	4.94	1.5	226.2	-	1.48
	3	3	1.523	2	2	1.298	2	2	2	2	2	1.77	2	2	1.776	3	3	1	4	-	-
Sodium Na^+	Na_2CO_3			$NaHCO_3$			$NaOH$			$NaCHO_2$			$NaC_2H_3O_2$			$Na_2C_2O_4$			$Na_3C_6H_5O_7$		
	105.99	23.49	2.54	84.01	9.34	2.2	40.0	50	2.13	68.01	48.69	1.92	82.03	33.51	1.528	134	3.48	3.61	258.1	-	-
	3	1.9	1.393	2	2	1	2	2	1.7	2	2	1.687	2	2	1.525	3	3	1	4	-	-
Potassium K^+	K_2CO_3			$KHCO_3$			KOH			$KCHO_2$			$KC_2H_3O_2$			$K_2C_2O_4 \cdot 1H_2O$			$K_3C_6H_5O_7$		
	138.21	52.61	22.9	100.1	25.78	2.17	56.11	54.75	2.044	84.12	76.80'	1.91	98.14	72.9	1.57	184.2	26.68	2.13	306.4	-	-
	3	3	1.545	2	2	1.411	2	2	1.738	2	2	1.885	2	2	1.863	3	3	1.25	4	-	-
Calcium Ca^{2+}	$CaCO_3$			---			$Ca(OH)_2$			$Ca(CHO_2)_2$			$Ca(C_2H_3O_2)_2$			CaC_2O_4			$Ca_3(C_6H_5O_7)_2$		
	100.09	0.0007	2.83	-	-	-	74.09	0.16'	2.2	130.1	14.24'	2.02	158.2	-	1.5	128.1	.0006'	2.2	498.4	-	-
	2	2	1	-	-	-	3	3	1	3	3	1	3	-	-	2	2	1	5	-	-
Magnesium Mg^{2+}	$MgCO_3$			---			$Mg(OH)_2$			$Mg(CHO_2)_2 \cdot 2H_2O$			$Mg(C_2H_3O_2)_2$			MgC_2O_4			$Mg_3(C_6H_5O_7)_2$		
	84.314	0.018'	3.05	-	-	-	58.32	.0007'	2.37	150.4	-	-	142.4	39.61	1.5	112.3	-	-	451	-	-
	2	2	1	-	-	-	3	3	1	3	-	-	3	3	1.421	2	-	-	5	-	-
Iron(II,III) Fe^{2+}, Fe^{3+}	$FeCO_3$			---			$Fe(OH)_3$			$Fe(CHO_2)_3$			$FeOH(C_2H_3O_2)_2$			$Fe_2(C_2O_4)_3$			$FeC_6H_5O_7 \cdot 5H_2O$		
	115.85	.00006	3.9	-	-	-	106.9	-	3.12	190.9	45.21'	-	190.9	-	-	375.8	-	-	335	-	-
	2	2	1	-	-	-	4	-	-	4	4	1.354	4	-	-	5	-	-	2	-	-
	Ammonia			Acetone			Methanol			Ethanol			D-Fructose			D-Mannitol			Sucrose		
	NH_3			$(CH_3)_2CO$			CH_3OH			CH_3CH_2OH			$C_6H_{12}O_6$			$C_6H_{14}O_6$			$C_{12}H_{22}O_{11}$		
	17.031	30	0.696	58.08	10	0.785	32.04	100	0.791	46.07	100	0.789	180.2	48	1.6	182.2	15	1.489	342.3	80	1.581
	1	1	1.778	3	3	1	2	2	2	3	3	1.824	6	6	1.204	11	11	1	11	11	1.163

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Table 2. “Tabulated” relative humidity of deliquescence (RHD) as used in various EQMs (see text for details). Values of those compounds of Table 1 are listed which are currently used. All values correspond to T=298 K.

	PO ₄ ³⁻	SO ₄ ²⁻	HSO ₄ ⁻	NO ₃ ⁻	Cl ⁻	Br ⁻	I ⁻	CO ₃ ²⁻	HCO ₃ ⁻	OH ⁻	CHO ₂ ⁻	C ₂ H ₃ O ₂ ⁻	C ₂ O ₄ ²⁻	C ₆ H ₅ O ₇ ³⁻
H ⁺	--	--	--	--	--	--	--	--	--	--	--	--	--	--
NH ₄ ⁺	--	0.7997	0.4000	0.6183	0.7710	--	--	--	--	--	--	--	--	--
Na ⁺	--	0.9300	0.5200	0.7379	0.7528	--	--	0.8977	0.9640	--	--	--	--	--
K ⁺	--	0.9751	--	0.9300	0.8426	--	--	--	--	--	--	--	--	--
Ca ²⁺	--	0.9700	--	0.4906	0.2830	--	--	--	--	--	--	--	--	--
Mg ²⁺	--	0.8613	--	--	0.3284	--	--	--	--	--	--	--	--	--
Fe ³⁺	--	--	--	--	--	--	--	--	--	--	--	--	--	--
	--	--	--	--	--	--	--	--	--	--	--	--	--	--

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Table 3. Calculated RHD based on ν_w from measured solubility and effective dissociation (ν_e) according to Eq. (21). Note that values are given when solubility measurements were available (listed in Table 1) and that these values strongly depend on the solubility values.

	PO ₄ ³⁻	SO ₄ ²⁻	HSO ₄ ⁻	NO ₃ ⁻	Cl ⁻	Br ⁻	I ⁻	CO ₃ ²⁻	HCO ₃ ⁻	OH ⁻	CHO ₂ ⁻	C ₂ H ₃ O ₂ ⁻	C ₂ O ₄ ²⁻	C ₆ H ₅ O ₇ ³⁻
H ⁺	0.0011	0.0939	--	0.7816	0.6908	0.8366	0.8886	--	--	0.0000	0.4370	0.7818	0.9400	0.0784
NH ₄ ⁺	0.8581	0.7980	0.3999	0.6067	0.7659	0.7839	0.7572	0.2182	0.8610	0.0019	0.5907	0.6387	0.9960	--
Na ⁺	0.9985	0.9390	0.9285	0.7476	0.7540	0.7713	0.7593	0.9051	0.9486	0.5160	0.6732	0.7965	0.9989	0.5927
K ⁺	0.1699	0.9827	0.8836	0.9279	0.8429	0.8363	0.8075	0.3334	0.8704	0.5850	0.5154	0.5964	0.8187	--
Ca ²⁺	--	1.0000	--	0.4806	0.3228	0.3922	0.4559	--	--	--	0.8990	--	--	--
Mg ²⁺	--	0.8950	--	0.7161	0.3508	0.4945	0.5676	--	--	--	--	0.5117	--	--
Fe ³⁺	--	0.0060	--	0.3338	0.1126	0.0248	0.9992	--	--	--	0.1994	--	--	--
	0.9415	0.7255	0.0018	0.0000	0.0032	0.8776	0.0000	--	--	--	--	--	--	--

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Osmosis - Pfeffer cell

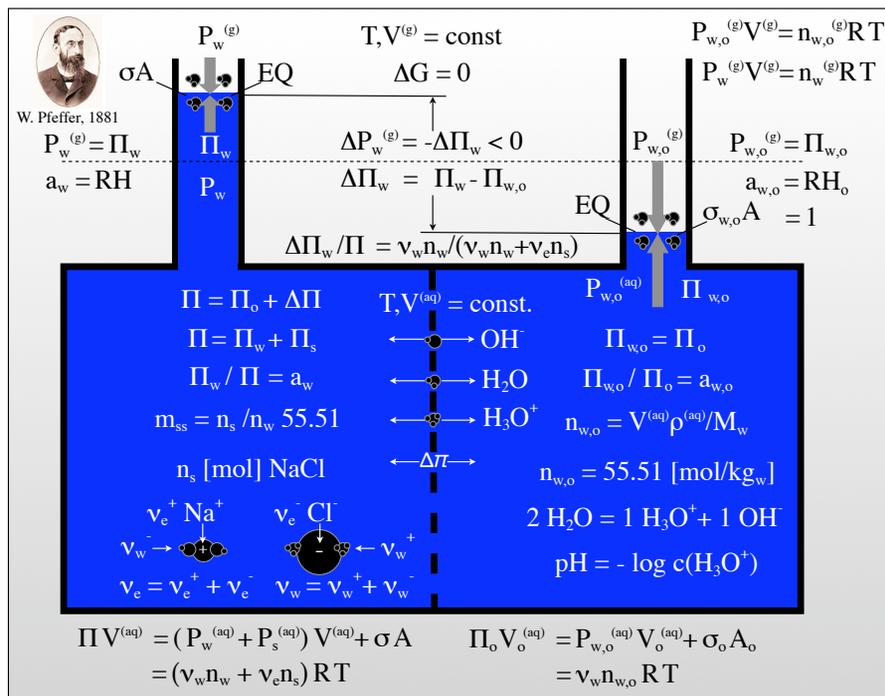


Fig. 1. (a) Laboratory conditions: schematic of an osmotic system.

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Aerosol water uptake

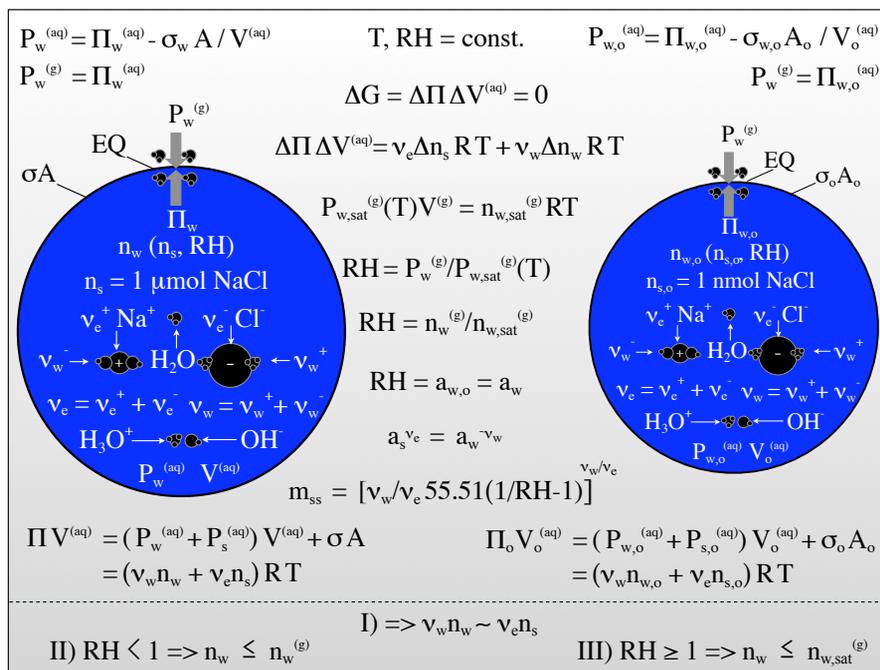


Fig. 1. (b) Atmospheric conditions: schematic of aerosol water uptake.

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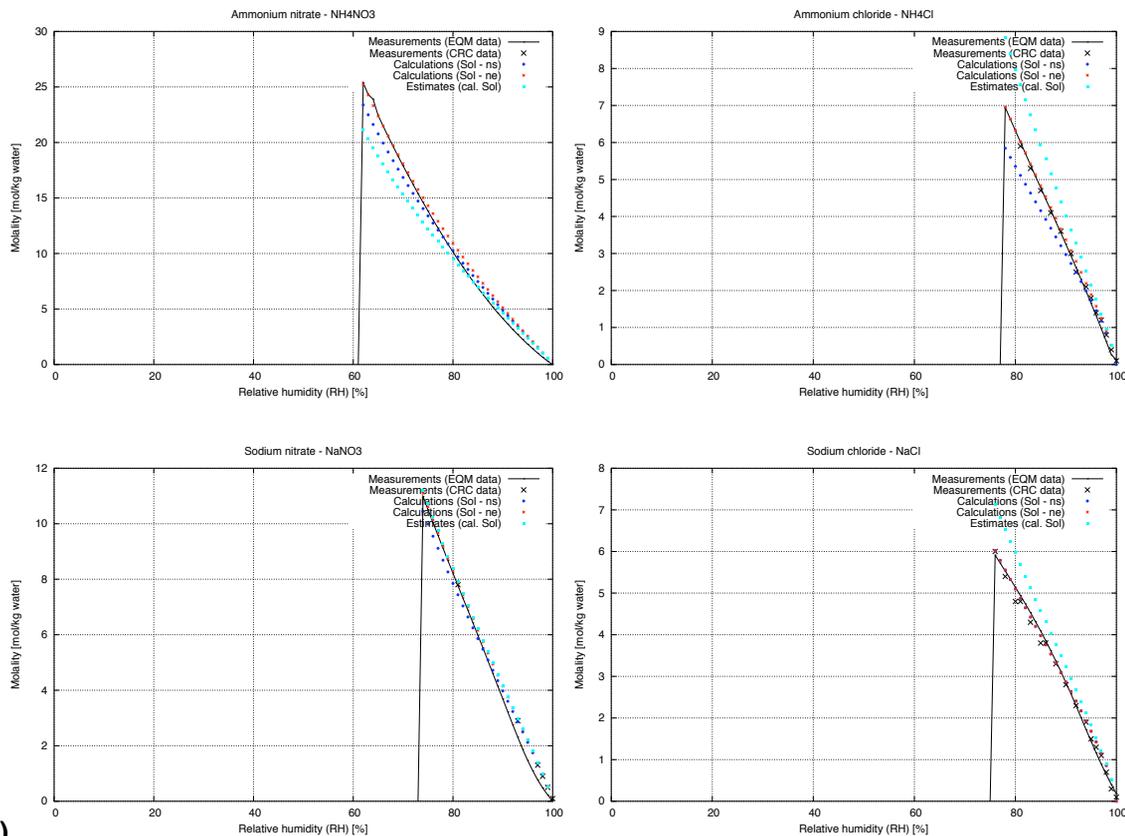
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Fig. 2. (a) Single solute molalities, (b) associated water mass (aerosol water uptake). Shown is a selection of figures presented in the electronic supplement (<http://www.atmos-chem-phys-discuss.net/7/849/2007/acpd-7-849-2007-supplement.zip>, Fig. A1).

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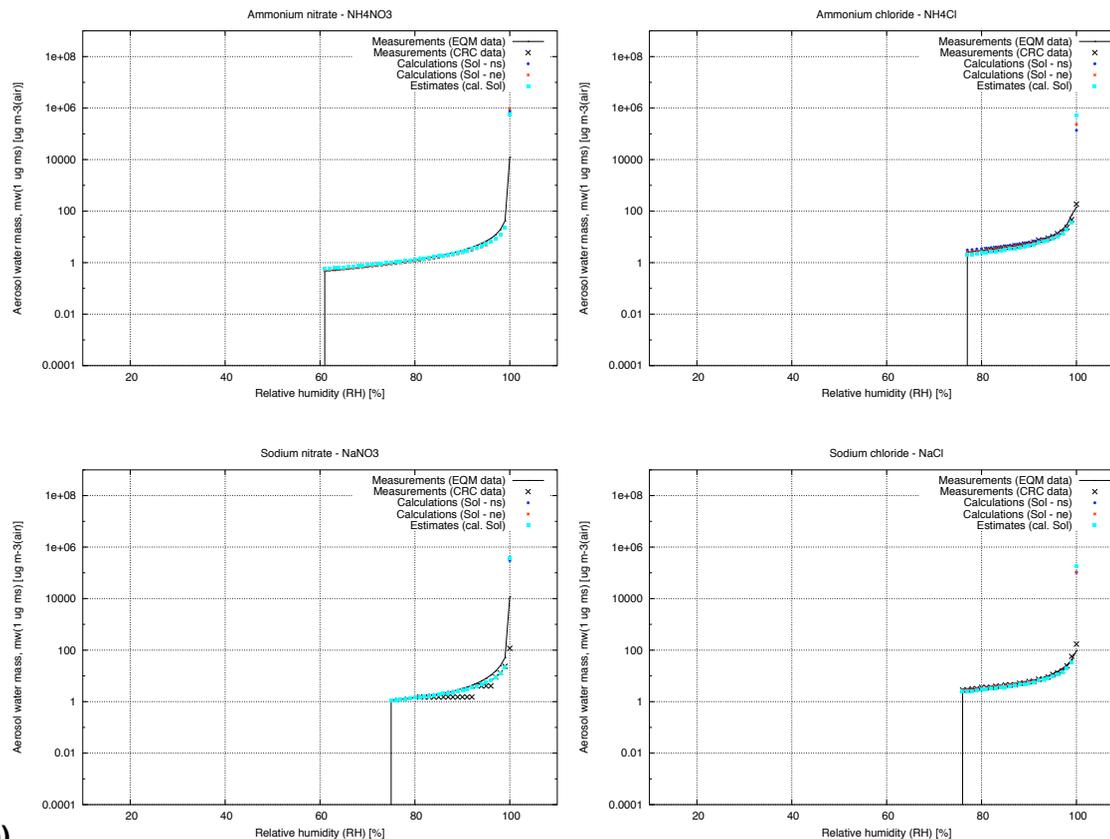
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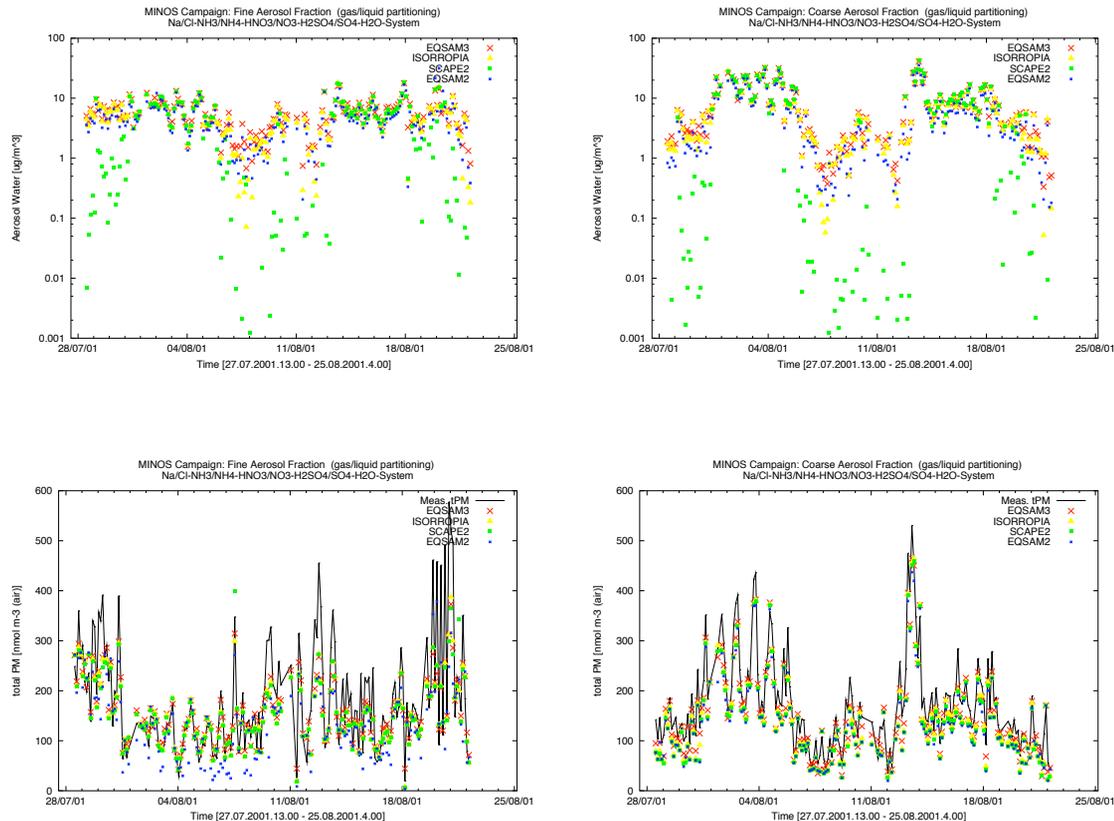
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Fig. 3. Mixed solution properties and model comparison for the MINOS campaign (Metzger et al., 2006). **(a)** Aerosol associated water (top), total number of moles of particulate matter (PM) (bottom) for fine (left) and coarse mode (right); **(b)** fine mode: total aerosol mass (top, left), total solid mass (top, right), aerosol ammonium nitrate activity coefficient (bottom, left), pH (bottom, right); **(c)** residual gaseous ammonia (top, left), residual gaseous nitric acid (top, right), aerosol fine mode ammonium (bottom, left), aerosol fine mode nitrate (bottom, right). All panels show time series for the period 28 July–25 August 2001 of the ammonium/sulfate/nitrate/chloride/sodium/water system, comparing measurements (black solid line) and results of EQSAM3 (red crosses), ISORROPIA (yellow closed triangles), SCAPE2 (green closed squares), EQSAM2 (blue, small crosses). Note that this model comparison and chemical system is identical to the model comparison for chemical system F2/C2 of Metzger et al. (2006) with EQSAM2 denoted there EQSAM2*.

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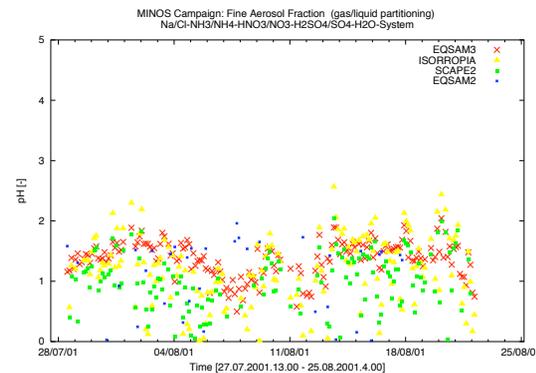
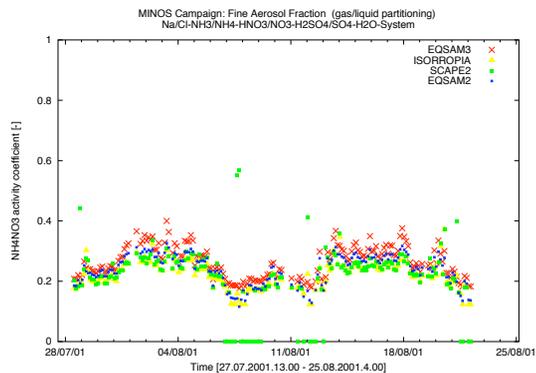
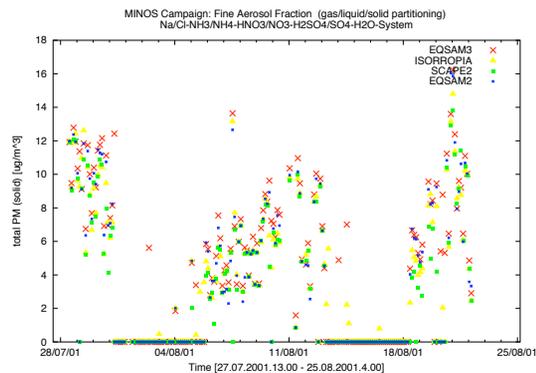
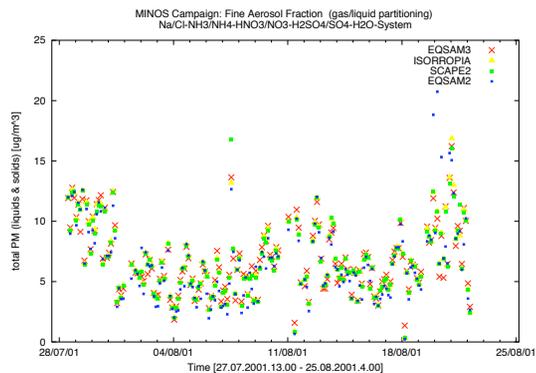
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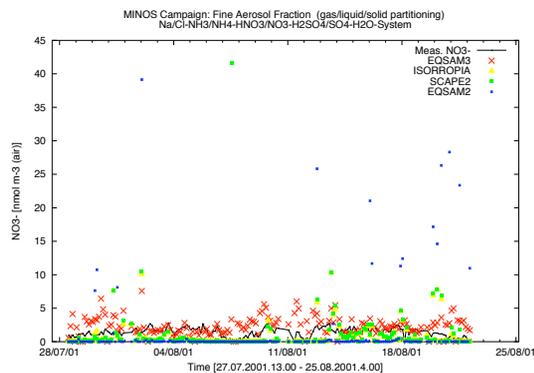
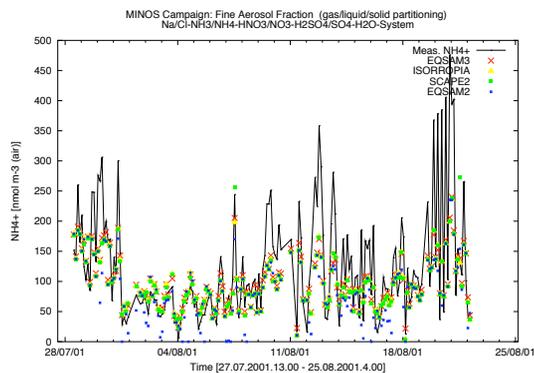
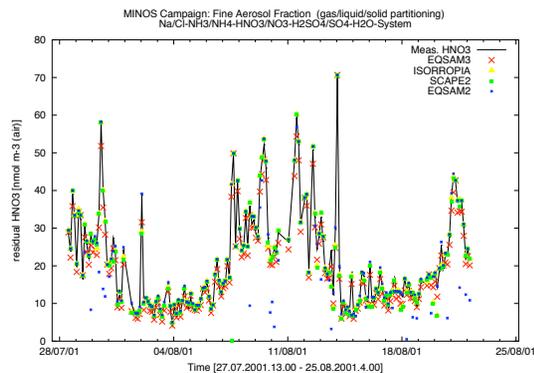
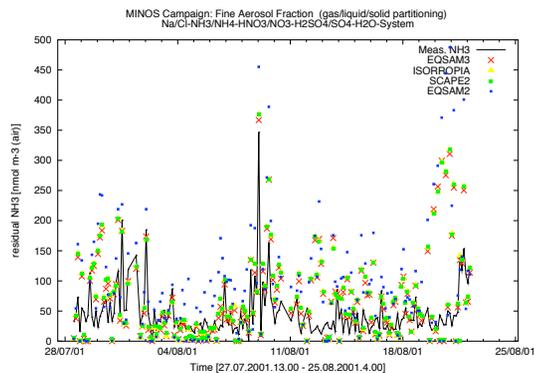
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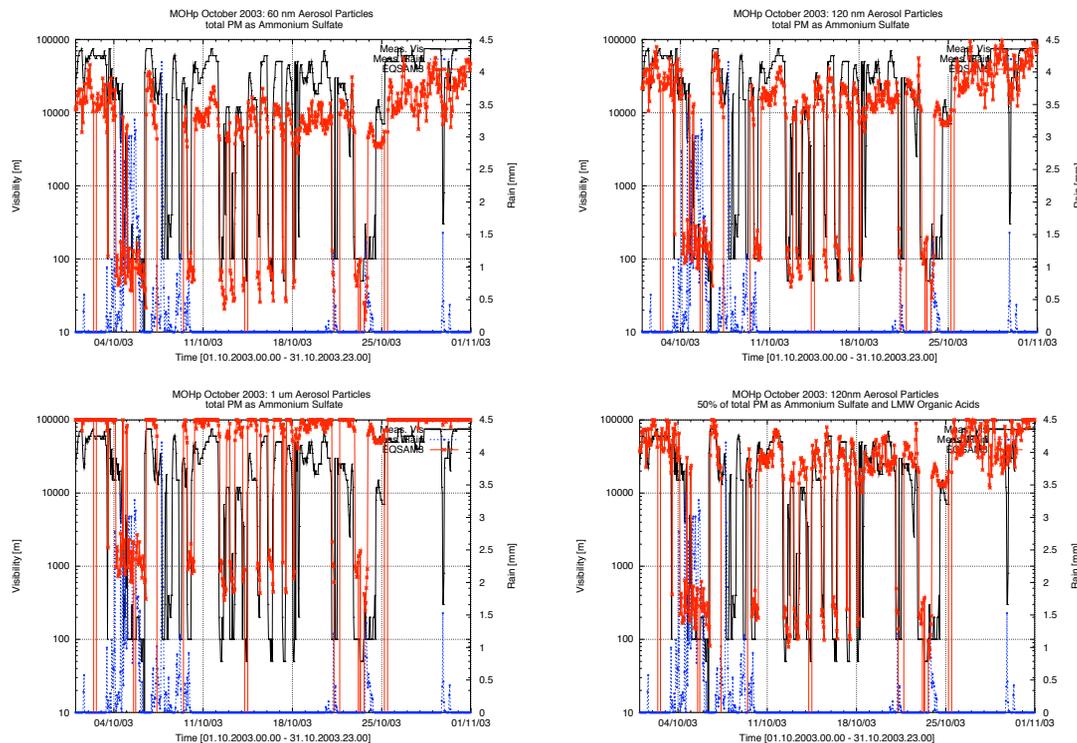


Fig. 4. Outlook: Visibility predictions with EQSAM3 (red) assuming different aerosol hygroscopicity and size: 60 nm particles ammonium sulfate (AS) (top, left), 120 nm particles AS (top, right), 1 μm particles AS (bottom, left), 120 nm particles with 50% AS and low molecular weight (LMW) organic acids (bottom, right). Visibility measurement of the Meteorological Observatory Hohenpeißenberg (MOHp), Germany are shown for October 2003 in black (solid line), precipitation (right y-axes) in blue (dotted).

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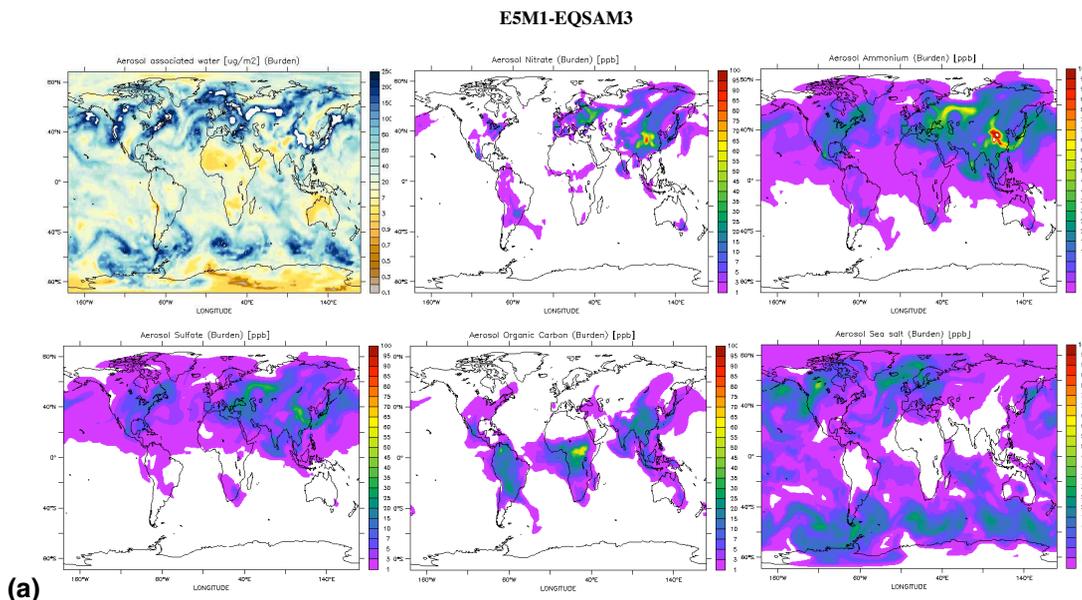


Fig. 5. Outlook: Global aerosol distributions for GMT noon 9. September 2000 (snap shot): **(a)** Atmospheric burden (fine mode): Aerosol associated water mass (AW) in $[\mu\text{g}/\text{m}^2]$, aerosol nitrate, ammonium, sulfate, primary organics and sea salt (from top left to bottom right); AW **(b)** tropospheric burden; **(c)** AW upper troposphere lower stratosphere (UTLS); **(d)** cloud coverage derived from AW; **(e)** cloud cover comparison for the US: standard calculations (top left), AW based (regional selection of panel d), satellite observations (GEOS, channel 4). The global calculations were obtained with the chemistry-climate model E5M1 (<http://www.messy-interface.org>).

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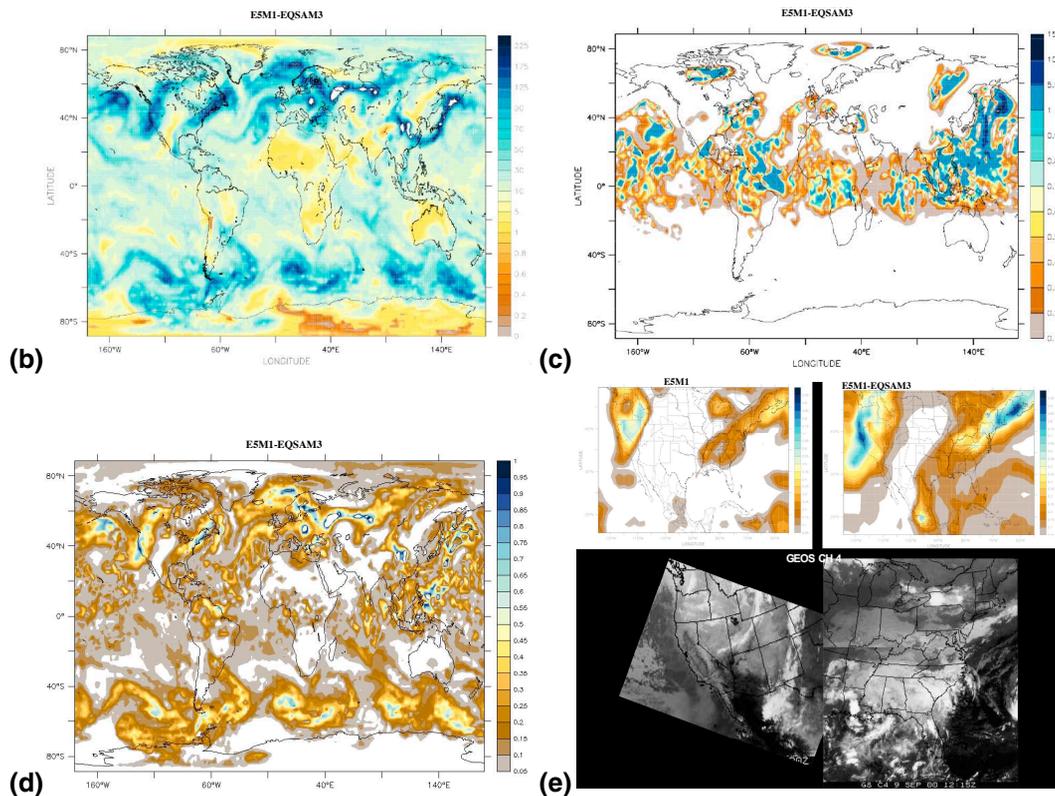


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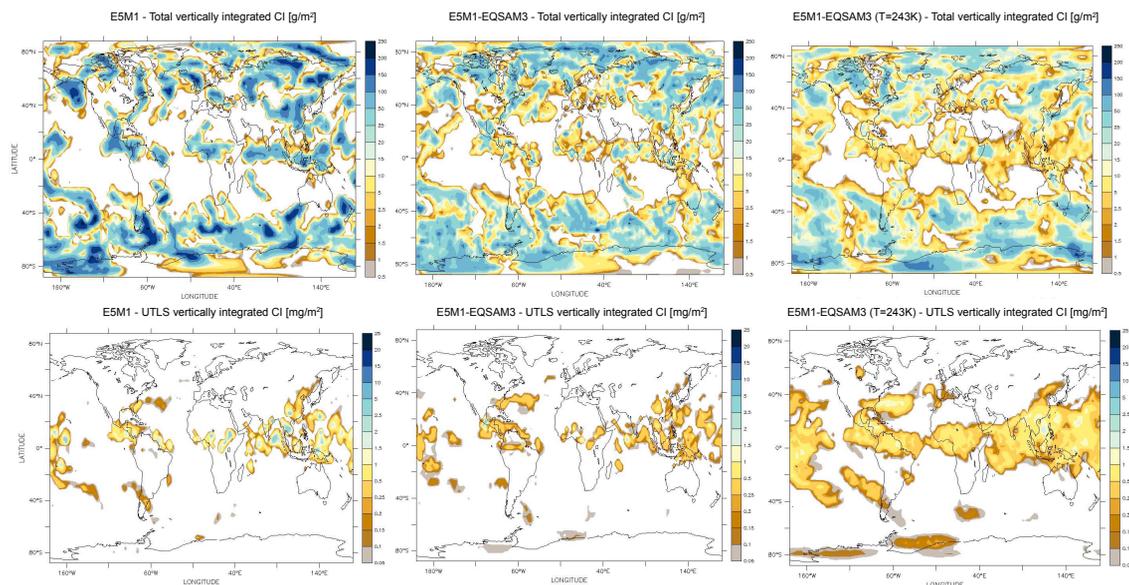


Fig. 6. Comparison of cloud ice content predictions – burden (top) UTLS (bottom): standard calculations (left), based on AW and PM with and explicit freezing point depression (middle), based on AW and PM with fixed freezing point ($T=243$ K). Model similar to Fig. 5.

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