Description of EQuSAM4: gas-liquid-solid partitioning model for global simulations

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Received: 28 September 2011 – Accepted: 20 October 2011 – Published: 24 October 2011
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Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

We introduce version 4 of the EQuilibrium Simplified Aerosol Model (EQUSAM4), which is part of our aerosol chemistry-microphysics module (GMXe) and chemistry-climate model (EMAC). We focus on the relative humidity of deliquescence (RHD) based water uptake of atmospheric aerosols, as this is important for atmospheric chemistry and climate modeling, e.g. to calculate the aerosol optical depth (AOD). Since the main EQUSAM4 applications will involve large-scale, long-term and high-resolution atmospheric chemistry-climate modeling with EMAC, computational efficiency is an important requirement. EQUSAM4 parameterizes the composition and water uptake of multicomponent atmospheric aerosols by considering the gas-liquid-solid partitioning of single and mixed solutes. EQUSAM4 builds on analytical, and hence CPU efficient, aerosol hygroscopic growth parameterizations to compute the aerosol liquid water content (AWC). The parameterizations are described in the companion paper (Metzger et al., 2011) and only require a compound specific coefficient $\nu_i$ to derive the single solute molality and the AWC for the whole range of water activity ($a_w$). $\nu_i$ is pre-calculated and applied during runtime by using internal look-up tables. Here, the EQUSAM4 equilibrium model is described and compared to the more explicit thermodynamic model ISOR-ROPIA II. Both models are imbedded in EMAC/GMXe. Box model inter-comparisons, including the reference model E-AIM, and global simulations with EMAC show that gas-particle partitioning, including semi-volatiles and water, is in good agreement. A more comprehensive box model inter-comparison of EQUSAM4 with EQUISOLV II is subject of the revised publication of Xu et al. (2009), i.e. Xu et al. (2011).

1 Introduction

The most comprehensive description of hygroscopic particle growth of atmospheric aerosols is provided by models that calculate the full gas-liquid-solid partitioning, i.e. the composition and state of the aerosol over the wide ranges of temperature and
relative humidity from the surface to the winter polar stratosphere. Since thermodynamic equilibrium is the final state of kinetic processes, many modeling approaches assume equilibrium, which is reasonable if the atmospheric processes that lead to

toward it are fast compared to those that lead away from it (Wexler and Potukuchi, 1998).

However, thermodynamic equilibrium is only a good assumption for aerosols with radii

up to 1 [µm] (Meng and Seinfeld, 1996). For larger particles there is a need to

account for the mass-transport related decrease in the aerosol concentration of semi-

volatile compounds (Pilinis et al., 2000; Feng and Penner, 2007). To calculate the

multiphase partitioning, composition and associated water uptake of multicomponent

atmospheric aerosols, various equilibrium models (EQMs) have been developed over

the past decades including: EQUIL (Bassett and Seinfeld, 1983), KEQUIL (Bassett and

Seinfeld, 1984), MARS (Saxena et al., 1986), MARS-A (Binkowski and Shankar, 1995),

SEQUILIB (Pilinis and Seinfeld, 1987), SCAPE (Kim et al., 1993a, b; Kim and Sein-

feld, 1995), SCAPE2 (Meng et al., 1995), EQUISOLV (Jacobson et al., 1996), EQUI-

SOLV II (Jacobson, 1999), AIM (Wexler and Seinfeld, 1991), AIM2 and E-AIM (Wexler

and Clegg, 2002), ISORROPIA (Nenes et al., 1998, 1999), ISORROPIA II (Fountoukis

and Nenes, 2007), GFEMN (Ansari and Pandis, 1999, 2000), EQSAM (Metzger et

al., 2002a, b), EQSAM2 (Metzger et al., 2006; Trebs et al., 2005), EQSAM3 (Metzger

and Lelieveld, 2007; Metzger et al., 2010), HETV (Makar et al., 2003), ADDEM (Top-

ping et al., 2005a, b), MESA (Zaveri et al., 2005), UHAERO (Amundson et al., 2006)

and AIOMFAC (Zuend et al., 2011). These models vary in their degree of complex-

ity and computational approaches. Almost all EQMs are computationally expensive,

since numerical accuracy often has higher priority than computational efficiency, so

that even the iterations to reach equilibrium are extensive and/or the computational

approaches are comprehensive. Practically, only three EQM types are computationally

efficient and widely applied in 3-D atmospheric chemistry modeling, i.e. MARS, ISOR-

ROPIA and EQSAM. These models are applied in different versions and often linked
to an aerosol microphysics module, embedded in either a Chemistry-Transport Model,
CTM (Metzger, 2000; Metzger et al., 2002a, b; Myhre et al., 2006; Tsigaridis et al.,

2006; Feng and Penner, 2007), or a General-Circulation Model, GCM (e.g. Adams et

al., 2001; Jacobson, 2001; Liao et al., 2003; Martin et al., 2004; Rodríguez and Dab-
dub, 2004; Lauer et al., 2005; Liao and Seinfeld, 2005; Liao et al., 2006; Bauer et

al., 2007a, b; Luo et al., 2007; Metzger et al., 2007; Pringle et al., 2010; Brühl et al.,

2011; Pozzer et al., 2011). However, despite the model development history of EQMs,

computational efficiency combined with accuracy and flexibility regarding the number

of chemical compounds that can be considered remains to be a key development in
global atmospheric aerosol-chemistry-climate modeling.

Here we introduce version 4 of the EQuilibrium Simplified Aerosol Model (EQSAM4),

which is part of an aerosol chemistry-microphysics module (GMXe) and a chemistry-

climate model (EMAC). Section 2.1 describes the EQSAM4 parameterization of the

composition and water uptake of multicomponent atmospheric aerosols, by consider-

ing the gas-liquid-solid partitioning of single and mixed solutes. The analytical, and

hence CPU efficient, single solute parameterizations are summarized in Sect. 2.2, de-

scribed in greater detail in the companion paper (Metzger et al., 2011, abbreviated in

the following as M2011). The corresponding mixed solution parameterizations and the

computational algorithm are summarized in Sects. 2.3. and 2.4, respectively. Sec-

tion 3.1 presents box model applications of EQSAM4 and the more explicit thermody-
u

amic reference model E-AIM for major single salt solutions (i.e. containing NaCl,

NH4NO3, NH4Cl, (NH4)2SO4, NH4HSO4, Na2SO4, NaNO3), and the corresponding

mixed solutions. Section 3.2 complements the box model results with results of a

global modeling application of EQSAM4 and ISORROPIA II, with both models imbed-

ded in EMAC/GMXe. We conclude with Sect. 4. For a more comprehensive box model

inter-comparison of EQSAM4 and other EQMs we refer to the revised publication of Xu

et al. (2009), i.e. Xu et al. (2011).
2 Model description

Version 4 of the EQuilibrium Simplified Aerosol Model (EQSAM4) is a solubility based gas-liquid-solid equilibrium partitioning model and a major revision of EQSAM3 with many improvements, although the overall analytical structure of EQSAM3 (Metzger et al., 2007) is largely unchanged. In contrast to other thermodynamic gas/aerosol equilibrium models, only a minimum number of iterations are required to solve the equilibrium reactions and the gas-liquid-solid partitioning of single solute or mixed solutions. Moreover, all relevant solution properties such as the solute molality (\(\mu_s\)), activity coefficients of (semi-)volatile compounds (\(\gamma_v\)), relative humidity of deliquescence (RHD), relative humidity of crystallization or efflorescence (RHE) and the associated aerosol water of binary and multi-component aerosol mixtures are parameterized using analytical functions, which depend at a specific relative humidity (RH) and temperature (T) only on a single solute specific coefficient \(v_i\) is pre-calculated at the model start from the chemical compound’s T-dependent RHD and saturation solubility \(\mu_{sat}^{i}\), and applied during runtime by using compound and T-dependent internal look-up tables of \(v_i\).

A key-feature of the EQSAM4 parameterizations is that the solute molality does not depend on the water content of the solution. Therefore, all solution properties can be calculated at a given RH and T only once for each compound, independent of whether single or mixed solutions are involved. During model set up all compounds can be individually switched on or off, and during run-time only the selected compounds are considered in internal compound loops. Calculations are skipped if a compound cannot form, e.g. because the required cation or anion has zero concentration. Both options can significantly enhance speed in global modeling applications, while the open architecture allows the user to easily incorporate new compounds or modify existing ones. The compounds currently implemented are listed in Table 1. EQSAM4 is positive-definite, mass- and charge-conserving, and considers the so-called hysteresis loop for aerosols that transfer between dry and moist environments.

For the hysteresis loop we assume that atmospheric aerosols (i) instantaneously take up water when solids deliquesce, i.e. in case the RH increases above the RHD of individual solid compounds (following the lower bound of the hysteresis loop), while (ii) aerosol water evaporates until crystallization occurs at the RHE point (following the upper bound of the hysteresis loop); at lower RH the aerosol water decreases instantaneously to zero. At the RHD, the solution is saturated and supersaturated at lower RH. An electrolyte is assumed solid when the RH is below its RHD (deliquescence branch) or RHE (efflorescence branch) when the solid precipitates from solution, whereas a solid is not allowed to form when the RH increases above the RHD or RHE, respectively. In both cases (efflorescence or deliquescence), the solute concentration increases with decreasing RH and decreasing aerosol water, while the total aerosol liquid water content usually increases with increasing RH and constant solute concentration, or constant RH and increasing solute concentration (mass or number). The aerosol particle is assumed dry when the RH is below the lowest RHD (deliquescence branch) or RHE (efflorescence branch) of all solutes present in the mixed solution; and in transport modeling applications, if additionally the total aerosol water from the previous model time-step is zero.

2.1 Method of parameterizing the gas-liquid-solid partitioning

The single and mixed solution concentrations are calculated by considering a neutralization reaction order, assuming chemical and thermodynamical equilibrium. The neutralization reaction order is automatically pre-determined during model start up for the selected species, which are considered in the gas-liquid-solid equilibrium partitioning calculations. The neutralization reaction order is based on the so-called salting-out effect of salt solutes and accounts for the order and degree to which ions bind water (Hofmeister, 1988). Two options are available:

1. Prescribed according to an adopted (T-independent) Hofmeister series;
2. Automatically determined based on the solute’s T-dependent RHD or RHE values.
For (2) the neutralization order is automatically determined for a given temperature using the $T$-dependent RHD values of the selected electrolytes. The electrolyte with the lowest solubility (highest RHD) is assumed to be neutralized first. For both options the compounds with highest RHD precipitates from the solution first so that the solute ions (of the precipitating compound) are not available for further reactions. For the RHE order, the procedure is basically the same, only the ranking of salt solutes varies. On the other hand, if the reaction order is prescribed as in (1), the following constant ($T$-independent) ranking is assumed, in which the ions to the left are neutralized preferentially, i.e.:

- Anions: $\text{PO}_{4}^{3-} > \text{SO}_{4}^{2-} > \text{HSO}_{4}^{-} > \text{NO}_{3}^{-} > \text{Cl}^{-} > \text{Br}^{-} > \text{I}^{-} > \text{CO}_{3}^{2-}
\text{HCO}_{3}^{-} > \text{OH}^{-} > \text{CHO}_{2}^{-} > \text{C}_{2}\text{H}_{5}\text{O}_{2}^{-} > \text{C}_{2}\text{O}_{4}^{2-} > \text{C}_{6}\text{H}_{5}\text{O}_{3}^{2-}$

- Cations: $\text{Fe}^{3+} > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{Na}^{+} > \text{K}^{+} > \text{NH}_{4}^{+} > \text{H}^{+}$

This ranking is based on Hofmeister (1988) and our modeling experience. It assumes that the neutralization of compounds approximately follows their ability to precipitate from a mixture of solutes. This increases the effective concentration of the remaining ions so that they precipitate if saturation is reached, e.g. in case of decreasing RH and water activity. The advantage of the prescribed neutralization order is that the ranking can be varied very easily (e.g. to study the effect on the overall gas-aerosol partitioning), but there is no $T$-dependency, while the RHD (or RHE) order automatically involves a $T$-dependency, which is applied during runtime for the compounds for which data is available (see Sect. 2.2 for details). An inter-comparison between these two neutralization orders is presented in the revised publication of Xu et al. (2009, 2011).

For both options, all salt solutes (cation-anion pairs) considered are ranked with respect to the preferred cation-anion neutralization and this index information is stored in an internal array, which is subsequently used as a look-up table during runtime, e.g. to obtain the corresponding ion and ion charge indices of the forming compounds (assuming charge balance). Then, during runtime, this index information is used for a given set of input cation and anion concentrations, $T$ and RH to neutralize first the cation-anion pair of the preferred compound, and from the remaining cation and anion concentrations the next compound. This procedure is repeated until all neutralization reactions of the selected compounds are solved. During this stage, only the input cation and anion concentrations change. EQSAM4 can consider approximately 100 compounds, listed in Table 1, though if fewer compounds are chosen, the number of compound loops is decreased. Since the resulting ion concentrations are used to solve the remaining neutralization reactions, an excess of cations or anions can remain. Any excess anions are then considered as non-neutralized acids, while excess cations are considered as hydroxides.

The partitioning between the solid and liquid phase is subsequently computed in the next (second) step based on the compound RHD (deliquescence branch) or RHE (efflorescence branch) values in case of single solute solutions. In case of mixed solutions, the corresponding mixed RHD (or RHE) values are used, which are calculated from the RHD (or RHE) of the single solutes present in the mixed solution (see Sect. 2.2 for details). The solutes then become solids in case the RH is below the RHD (deliquescence branch) or RHE (efflorescence branch) value. In the third step, water vapor from the air is supplied to the solution mixture (instantaneously) to account for the $\text{H}^{+}$ and $\text{OH}^{-}$ required to neutralize the compound mixture and conserve mass.

The partitioning between the gas and aqueous phase is parameterized in step four for the acids, using compound specific and RH-dependent parameterization of activity coefficient (see Sect. 2.2 for details). In the final (fifth) step, the diagnostic EQSAM4 output such as total masses in each phase, or aqueous solution properties are calculated such as the total water content, pH, and the ionic strength of the solution. The water content is calculated for all aqueous solutes, and subsequently the pH from the total water content and the final $\text{H}_{2}\text{O}^{+}$ and $\text{OH}^{-}$ concentrations. Note that in contrast to most EQMs, these aqueous solution properties are not required to determine the single or mixed solution concentrations.
2.2 Single solute parameterizations

The EQSAM4 parameterizations are a function of the solute specific coefficient $\nu_i$ and RH.

### 2.2.1 The RH of deliquescence (RHD) and efflorescence (RHE) as a function of $\nu_i$

It is assumed that atmospheric aerosols absorb water vapor if the RH rises above the dimensionless relative humidity of deliquescence (RHD), or desorb water vapor until the RH decreases below the dimensionless relative humidity of efflorescence (RHE). The RHD refers to an equilibrium RH at which a dry and crystalline salt compound completely deliquesces due to water vapor uptake at sufficiently high RH. At the lower end the RHE refers to an equilibrium RH at which an aqueous (and potentially dissociated) salt compound completely dries again, i.e. it crystallizes due to evaporative loss of water at sufficiently low RH. Assuming equilibrium and solution saturation, it is implicit that phase partitioning takes place at RHD from entirely dry (and crystalline) to entirely wet (dissolved), and analogously for the RHE case. Thus, modeling the RHD and RHE can only approximate reality, since a non-equilibrium approach is not accounted for. Thus, any interim transition phase of single solutes is not considered, although they are to some degree captured by the modeling of mixed solutions (described in Sect. 2.3).

The RHD parameterization relates the solute solubility, i.e. the saturation molality of the dissolved solute, to RH by the solute specific coefficient $\nu_i$. According to Eq. (16b) of M2011, i.e. the (simplified) relation without the Kelvin-term is given by:

$$RHD = \left(1 + \mu_s^0 \cdot M_w \cdot \nu_i \cdot \left[\frac{1}{\mu_s^0} \cdot \frac{1}{M_s \cdot \left(\frac{1}{w_s} - 1\right)} + B_{98}\right]\right)^{-1}$$

The RHE is parameterized accordingly, following Metzger and Lelieveld (2007) as:

$$RHE = 1 - \left(1 + \mu_s^0 \cdot M_w \cdot \nu_i \cdot \left[\frac{1}{\mu_s^0} \cdot \frac{1}{M_s \cdot \left(\frac{1}{w_s} - 1\right)} + B_{98}\right]\right)^{-1}$$

$M_w$ and $M_s$ denote the molar mass [kg/mol] of water and solute, and $w_s$ [-] the mass fraction solubility. $\mu_s^0 = 1$ [mol(solute)/kg(H$_2$O)] and the term $B_{98}$ is:

$$B_{98} = 10^\left[\frac{x}{2} - 2\right] = x \cdot w_s$$

with $x$ an arbitrary variable used to relate $B_{98}$ and $w_s$; $x$ follows if $\nu_i$ is known. $\nu_i$ is determined in Sect. 2.2.2. $B_{98}$ refers to applications at RH $\leq 98$ [%,]. Note that the model default is using $B_{98}$ rather the complete A and B terms (defined in M2011 for which also the Kelvin-term is considered), since the $B_{98}$ term allows us to solve the equations analytically, i.e. without iterations. The model has an option to consider the Kelvin-term, which uses the complete A and B terms and pre-calculated values of the solute solubility (through look-up tables). This additional option is currently only validated for NaCl and (NH$_4$)$_2$SO$_4$ due to the lack of available data. This will be further investigated. Also note that the $B_{98}$ term yields similar results as the Kelvin-term option for the important RH range RHD $< RH \leq 98$ [%] (M2011).

To consider temperature dependency of the RHD and RHE values EQSAM4 applies the widely used $T$-dependency for major salt compounds (e.g. Wexler and Potukuchi, 1998):

$$RHD(T) = RHD(T_0) \cdot \exp\left[T_{\text{coeff}} \cdot \left(1 - \frac{1}{T} - \frac{1}{T_0}\right)\right]$$

For all compounds for which $T$-dependent RHD and $w_s$ data are not available, no $T$-dependency is considered per default. However, EQSAM4 has an option
to approximate a $T$-dependency for the solute solubility $w_s$ following Metzger and Lelieveld (2007), i.e.

$$w_s(T) = w_s(T_0) \cdot \frac{T}{T_0}$$

so that a $T$-dependency of the RHD can be calculated from Eqs. (5), (3) and (1), and for the RHE from Eqs. (5), (3) and (2). Only the default option explicitly accounts for different heat capacities of salt compounds by the use of $T$-coefficients. The $T$-coefficients and RHD values at $T_0 = 298 \, [K]$ are shown in Table 2 for compounds of which coefficients are available; values are the same as those used in ISORROPIA II (see Table 4 of Fountoukis and Nenes, 2007). RHD values at $T_0$ and $T$-coefficients are unfortunately only available for the major inorganic salt compounds listed in Tables 1 and 2. Data for organic salt compounds are lacking, and $T$-coefficients for the RHE are not available for both inorganic or organic salt compounds. We therefore have included the option to estimate a $T$-dependency of both RHD and RHE from a parameterized $T$-dependency of the solute solubility using Eq. (5). However, this option is considered only for test purposes (e.g. sensitivity studies) as it requires evaluation and further development. Also, all non-bold RHD and all RHE values shown in Tables 3 and 4 are optional and indicative though similar to Metzger and Lelieveld (2007), since measurements are required for validation, in particular for the RHE values. For instance, a shape factor is currently not applied, though required for certain compounds to crystallize at the observed RHE.

For example, the predicted RHE value of NaCl is higher than its RHD value, which can be corrected if a shape factor is applied. Thus, further improvement is foreseen. The RHE values corresponding to the compounds listed in Table 3 are partially evaluated in the revised publication of Xu et al. (2009, 2011). Missing compounds (Tables 3 and 4 compared to Table 1) are not considered for the liquid-solid-partitioning calculations, although they are included in the overall gas-aerosol partitioning (if selected), to account for their dry mass, which affects the overall hygroscopic growth factor and the derived aerosol size distribution and life-time.

2.2.2 Determination of $v_i$

The dimensionless solute specific coefficient $v_i$, [-] is obtained from the measured reference RHD (as used in Eq. 4) with the bisection method (described in Sect. 3 of M2011) for compounds for which a reference value is available, i.e. all compounds listed in Table 2. The same RHD values are indicated in bold in Table 3 (all values were re-calculated with Eq. 1 and are, in this case, identical to those of Table 2). For all compounds for which reference RHD values are not available, $v_i$ is obtained from the solute’s mass fraction solubility, $w_s$, following Metzger and Lelieveld (2007), by using Eq. (3) with $x=1$. Upon rearranging Eq. (3) yields:

$$v_i \approx \left( \frac{1}{2} \cdot \log_{10}(w_s) \right) + 1$$

Table 1 includes the pre-calculated $v_i$ and $B_{98}$ values. The estimated RHD and RHE values are shown in Tables 3 and 4, respectively (not bold). $v_i$ has been estimated from Eq. (6), by using the solubility measurements ($w_s$) and the required thermodynamic data shown in Table 1; all taken from the CRC Handbook of Chemistry and Physics (2006).

2.2.3 The solute molality $\mu_s$ as a function of RH and $v_i$

EQSAM4 applies Eq. (17d) of the companion paper (M2011), which parameterizes the solute molality $\mu_s$ [mol(solvent)/kg(H$_2$O)] as a function of $v_i$ and RH. For RH $\leq$ 98 [%], i.e.:

$$\mu_s = \mu_s^0 \cdot \left( \frac{1}{v_i \cdot \mu_s^0 \cdot M_i} \cdot \left( \frac{1}{\text{RH}} - 1 \right) \right)^{\nu_i} - B_{98}$$

Figure 1 shows the solute molality calculated with Eq. (7) as a function of water activity for major inorganic compounds. Note that the water activity here is equal to the
2.2.4 The activity coefficient $\gamma_s$ of semi-volatile species as a function of $v_i$ and RH

As outlined in the companion paper (M2011), $v_i$ substitutes activity coefficients for non-volatile solutes that only undergo solid-liquid partitioning. However, to parameterize the gas-liquid or gas-solid partitioning of (semi-)volatile solutes, an empirical relation between the solute molality $\mu_s$ and activity coefficient $\gamma_s$ is assumed as a function of RH and $v_i$, following Metzger et al. (2002a) and Metzger and Lelieveld (2007):

$$\gamma_s = \bar{Z}_s \cdot \left( \frac{\mu_{s,v}^0}{\mu_s} \right)^{0.5}$$  

(8)

Currently EQSAM4 applies $\gamma_s$ for only 2 of the approximately 100 compounds, i.e. for NH$_4$NO$_3$ where the (empirical) variable $Z_s = 0.7$, and NH$_4$Cl where $Z_s = 1.6$. Note that Eq. (8) accounts for a $T$-dependency, if $v_i$ is determined, e.g. with the bisection method and Eq. (1) using $T$-dependent RHD and $w_s$ data (as described in Sect. 3 of M2011). $\gamma_s$ is shown in Fig. (2) as a function of RH for NH$_4$NO$_3$ and NH$_4$Cl at $T = 298.15$ [K]. For NH$_4$Cl the saturation molality is used throughout the RH range, i.e. $\mu_{s,RH} = \mu_{s,RHD}$ is assumed to obtain $\gamma_s$ with Eq. (8). The parameterized $\gamma_s$ values are in reasonable agreement with the data used by ISORROPIA II and EQUISOLV II. A detailed evaluation is the subject of the revised publication of Xu et al. (2009, 2011), which presents a comprehensive model inter-comparison between EQSAM4 and EQUISOLV II. In Sect. 3, EQSAM4 is compared with ISORROPIA II and E-AIM.

2.2.5 The aerosol liquid water content (AWC)

The AWC of single solutions, $m_w\text{(single)}$ [kg/m$^3$(air)], can be obtained for a given solute concentration $n_s$ [mol/m$^3$ (air)] if the solute molality $\mu_s$ [mol(solute)/kg(H$_2$O)] is known:

$$m_w(\text{single}) = \frac{n_s}{\mu_s}$$  

(9)

In EQSAM4 $\mu_s$ is obtained from Eq. (7) using the pre-calculated solute specific coefficient $v_i$, so that Eq. (9) can be readily solved if $n_s$, $T$ and RH are known. Note that in contrast to other approaches, $\mu_s$ obtained from Eq. (7) does not depend on the total AWC of the solution, so that the AWC can be treated as a diagnostic property. This simplifies and speeds up calculations, notably for mixed solutions and global modeling applications.

2.3 Mixed solution parameterizations

EQSAM4 solves the gas-liquid-solid partitioning of mixed solutes non-iteratively by applying an additional parameterization using mean values $X_i$, which are generally calculated from:

$$\hat{X}_{i,j} = \frac{1}{N} \sum_{j=1,N} (X_{i,j})$$  

(10)

$X_{i,j}$ is the $i$-th of $i = 1,..,k$ variables of the $j$-th of $j = 1,..,N$ compounds present in the multicomponent solution (e.g. $v_i$, $w_s$, $B_{ij}$) and is used in the corresponding single-solute equation.

2.3.1 The mixed solution aerosol water content (MAWC)

The MAWC, $m_w(\text{mix})$ [kg/m$^3$(air)], is obtained from the ZSR-mixing rule (Stokes and Robison, 1966) and calculated from the sum of all partial water masses, obtained from
Eq. (9):

\[ m_{w(\text{mix})} = \sum_{j=1}^{N} m_{w(\text{single})} \]  

(11)

### 2.3.2 The mixed solution RHD

EQSAM4 has an option to consider a mean i.e. mutual RHD (MRHD) for mixed solutions, which is obtained from Eq. (1) by using the required mean values, following Metzger and Lelieveld (2007). The means are calculated from Eq. (10), but consider only the selected compounds that are dissolved (as described in Sect. 2.1):

\[
\text{MRHD} = \left(1 + \mu_s^0 \cdot M_w \cdot \tilde{\gamma}_j \cdot \left[ \frac{\mu_s^{\text{sat}}}{\mu_s^0} + B_{88} \right] \right)^{-1}
\]

(12)

\[ \tilde{\mu}_{s,j} = \frac{1}{N} \sum_{i=1}^{N} (\mu_{s,j}^{\text{sat}}) \]

The mixed solution RHD is considered as solids. Thus, the lowest RHD of the mixed compounds determines the onset of water uptake. However, since shape or other correction factors are not considered, the values are indicative (measurements are required for validation). EQSAM4 therefore considers per default the same mixed solution MRHD values as used in ISORROPRIA II if the composition matches the same pre-defined aqueous salt compositions listed in Table 5 of Fountoukis and Nenes (2007).

### 2.3.3 The mixed solution RHE

EQSAM4 also allows to consider a mean RHE (MRHE) for mixed solutions, which is obtained from Eq. (2) by using the required mean values, also following Metzger and Lelieveld (2007):

\[
\text{MRHE} = 1 - \left(1 + \mu_s^0 \cdot M_w \cdot \tilde{\gamma}_j \cdot \left[ \frac{\mu_s^{\text{sat}}}{\mu_s^0} + B_{88} \right] \right)^{-1}
\]

(13)

\[ \tilde{\mu}_{s,j}^{\text{sat}} = \frac{1}{N} \sum_{i=1}^{N} (\mu_{s,j}^{\text{sat}}) \]

Note that \( \mu_s^0 = 1 \) [mol(solute)/kg(H\(_2\)O)] has the same value as in Eq. (1). EQSAM4 considers all compounds of the mixed solution as aqueous when their RHD is higher than the mean RHD. These compounds with a RHD below the MRHD are considered as solids. Thus, the lowest RHD of the mixed compounds determines the onset of water uptake. However, since shape or other correction factors are not considered, the values are indicative (measurements are required for validation). EQSAM4 therefore considers per default the same mixed solution MRHE values as used in ISORROPRIA II if the composition matches the same pre-defined aqueous salt compositions listed in Table 5 of Fountoukis and Nenes (2007).

### 2.3.4 The mixed solution activity coefficient \( \gamma_{s(\text{mix})} \)

The mixed solution activity coefficient \( \gamma_{s(\text{mix})} \) is obtained from \( \gamma_s \) by applying domain specific (empirical) coefficients, \( x \) and \( y \) that alter the \( \gamma_s \) parameterization given by Eq. (8), i.e.:

\[ \gamma_{s(\text{mix})} = (y \cdot \gamma_s)^x \]  

(14)

For the two volatile compounds, NH\(_2\)NO\(_3\) and NH\(_2\)Cl, \( y = 1.725 \) and \( y = 1 \), respectively, and the corresponding \( x \) values are listed in Table 7. \( x \) in Eq. (14) is different from that in Eq. (3) and is determined for certain cation-anion ratios, i.e. mixed solution domains (D1–10), Table 5, which are in turn used to identify certain regimes (R1–6).
listed in Table 6. To parameterize the aqueous uptake of the residual gases (first row of Table 1 and \( \text{NH}_2 \)), the coefficients given in Table 8 are used. To obtain the dissolved fractions of semi-volatile compounds the ion concentrations are multiplied with the activity coefficients during the neutralization step. In principle there are 60 combinations possible, 10 domains listed in Tables 5 and 6 regimes per domain listed in Table 6. However, most combinations are currently not used. Only certain specific combinations of domains and regimes are applied to determine the activity coefficients for \( \text{NH}_2 \text{NO}_3 \), \( \text{NH}_2 \text{Cl} \) and the residual gases (i.e. first row of Table 1 and \( \text{NH}_2 \)), as shown in Tables 7 and 8, respectively. For the domains D1, D2, D3, D9 no specification according to Table 6 is needed and the following values are used: \( x_{\text{NH}_2 \text{NO}_3} = 2 \) and \( x_{\text{NH}_2 \text{Cl}} = 6 \) for Table 7, and \( x = 2 \) and \( y = 0.25 \) for Table 8. Note that Tables 7 and 8 are considered only for the activity coefficient calculation in mixed solutions and that Table 7 is required only for two compounds, while Table 8 becomes relevant only for high RH, i.e. if RH > 90 \(%\). Only under these conditions sufficient aerosol water is predicted to allow for the uptake of gases in aqueous solutions. However, at this RH cloud formation is usually assumed over some portion of the grid in GCMs and the uptake of gases is dominated by uptake in cloud droplets.

2.4 Computational algorithm

EQSAM4 solves the gas-liquid-solid partitioning of single and mixed solutes iteratively by applying a set of analytical equations through a solution independent and compound specific coefficient, \( \nu_i \). The analytical equations depend on \( \nu_i \) and RH and have been detailed in M2011. The EQSAM4 model general solution procedure can be subdivided into four main calculation steps as illustrated in Fig. 3, whereby only step three is executed during runtime:

1. Model initialization:
   
   (a) At start up the model reads the gas/aerosol input concentrations at the given \( T \) and RH.

   (b) The model complexity and speed (during runtime) can be controlled by various switches, e.g. compounds can be individually selected to minimize array sizes and the number of internal compound loops.

   (c) The compound specific arrays are initialized using the thermodynamic data provided in Table 1 for the selected compounds only.

2. Pre-calculation of \( T \)-dependent look-up tables that are accessed during runtime:

   (a) At the second step after model start up compound specific properties are pre-calculated and stored in internal look-up tables for a range of temperature \( T = 150–350 \,[\text{K}] \).

   (b) For compounds for which data is available the \( T \)-dependency of the RHD values are calculated from Eq. (4) using the \( T \)-coefficients provided in Table 2.

   (c) For the same compounds, the \( T \)-dependent solute solubility measurements, \( w_s(T) \) are applied. The \( w_s(T) \) values are taken from the CRC Handbook of Chemistry and Physics (2006) for 5 different temperatures in the range 273–313 \,[\text{K}] \) with a 10 \,[\text{K}] \) interval and a linear interpolation in-between, while for all other compounds listed in Table 1 no \( T \)-dependency is applied in the standard model set up. However, for test purposes (e.g. sensitivity studies) an internal switch exits to approximate a \( T \)-dependency using Eq. (5).

   (d) For the compounds listed in Table 2 the solute specific coefficient \( \nu_i \) is determined from Eq. (1) with the bisection method by using the \( T \)-dependent \( w_s \) and RHD data, while for all other compounds listed in Table 1 \( \nu_i \) is estimated from \( w_s \). The \( \nu_i \) values are shown in Table 1; the values are printed in bold if they are determined using Eq. (1), otherwise, they are approximated using Eq. (6). The \( B_{30} \) values are calculated from Eq. (3) and shown in Table 1; they equal \( w_s \) when \( \nu_i \) is estimated from Eq. (6).

   (e) The RHD and RHE values for all compounds are calculated from Eq. (1) and (2), respectively, using the \( T \)-dependent \( \nu_i \) and \( w_s \) lookup table data.
The RHD and RHE values are shown in Tables 3 and 4, respectively; bold RHD values indicate that the values are equal to those in Table 2 (they have been used to determine \( v_j \)). The \( T \)-dependency of the bold RHD data is the same as that applied in ISORROPIA II and shown in Fig. 2 of Fountoukis and Nenes (2007). For the default model setup no \( T \)-dependency is considered for the RHD values for all other salt compounds listed in Table 1, and no \( T \)-dependency is considered for all RHE values due to the lack of available measurements, except if a \( T \)-dependency of the solubility is optionally estimated with Eq. (5). The potentially \( T \)-dependent, RHD and RHE values are applied during runtime to solve the liquid-solid partitioning.

(f) In case the user has chosen that the neutralization reaction order is automatically pre-determined during model start up (in the standard model setup), the (optionally all \( T \)-dependent) RHD and RHE values of the selected compounds are ranked so that the array indices determine the neutralization reaction order.

(g) In case the neutralization reaction order is prescribed, a \( T \)-independent and predefined and ion specific ranking (see Sect. 2.1) is applied instead during runtime.

(h) In case the Kelvin-term is considered, the solute molality \( \mu_s \) is pre-calculated for the upper RH range, \( 0.98 < \text{RH} < 1.1 \) using \( T \)-independent \( v_j \) values, by solving the complete \( \mu_s \) equation, i.e. Eq. (17b) of M2011, with \( v_j \) determined at \( T = 298.15 \) [K]. The \( \mu_s \) values are stored in internal lookup-tables and accessed during runtime. For the lower RH range, \( 0 < \text{RH} < 0.98 \), \( \mu_s \) is calculated during runtime from Eq. (7).

3. Runtime calculations – gas/liquid/solid aerosol equilibrium partitioning:
   (a) The look-up tables the RHD, RHE, \( v_j \) and potentially \( \mu_s \) values are assigned to local arrays for the actual temperature and run-time arrays are initialized.

(b) All \( \text{RH} \)-dependent solute properties are calculated during runtime for a given \( \text{RH} \) and \( T \) for the selected compounds; i.e. the solute molality \( \mu_s \) is calculated for the lower RH range, \( 0 < \text{RH} < 0.98 \) from Eq. (7). Subsequently, \( \mu_s \) is used by Eq. (8) to obtain the activity coefficient \( \gamma_s \) for the two volatile compounds, \( \text{NH}_4\text{NO}_3 \) and \( \text{NH}_4\text{Cl} \), and for the gases that are considered for uptake in aqueous solutions, i.e. all compounds in the first row of Table 1 and \( \text{NH}_3 \).

(c) The neutralization reactions are solved and salt compounds are calculated from the neutralization of input cation and anion concentrations, with the reaction order either determined automatically, based on the optional \( T \)-dependent RHD or RHE values of the selected compounds, or prescribed (and \( T \)-independent). The reaction order is set to be automatic in the standard model setup.

(d) The aerosol water history determines whether the water uptake and the gas/liquid/solid aerosol equilibrium partitioning is calculated for the deliquescence or efflorescence branch of the hysteresis loop of salt compounds: (i) In case the AWC of the previous computation time step is zero (or below a user defined minimum) deliquescence is assumed and the neutralization reaction order is based on the ranking of the pre-calculated RHD values; (ii) Otherwise the pre-calculated RHE reaction order is applied. Alternatively, the neutralization reaction order can be prescribed, but is in this case \( T \)-independent.

(e) Compounds with the lowest solubility precipitate from solution at higher RH, so that these ions are not available for further reactions. For instance, the solubility of calcium sulfate (\( \text{CaSO}_4 \)) is very low (< 1 [%]) which practically leads to precipitation of \( \text{CaSO}_4 \) at a fractional RH close to 1, i.e. RHD = 0.9554 (Table 2). Once \( \text{CaSO}_4 \) is precipitated from the solution, the corresponding \( \text{Ca}^{2+} \) and \( \text{SO}_4^{2-} \) ions are taken from the solution and hence not available for further neutralization reactions. Then, from the remaining ion concentrations, the following salt compounds are formed and the non-neutralized “free” ions are computed. This procedure is repeated for all selected compounds, which
are kept in the aqueous phase at this stage.

(f) Bi-salts are specially treated to account e.g. for the fact that sulfate is preferentially neutralized compared to other anions such as nitrates and chlorides, because it is a stronger acid. This is inherent in the internal ranking of indices of the neutralization reaction order.

(g) For the two volatile salts, NH$_4$NO$_3$ and NH$_4$Cl, activity coefficients are considered for the compound neutralization, and the $T$-dependent equilibrium constants (same values as in ISORROPIA II and listed in Table 2 of Fountoukis and Nenes, 2007) are applied in the default model set up (these can be switched off for sensitivity tests). All other salt compounds are treated as non-volatile, and equilibrium constants and activity coefficients are not required (the solubility and $v_i$ act as a substitute). Non-volatile compounds remain in the particulate phase independent of the solute concentration, whereby the liquid/solid partitioning is determined by the solute solubility (through RHD or RHE). Since the water mass is proportional to the solute mass (at a given $T$ and RH), additional activity coefficients are not needed for non-volatile compounds; instead, the solubility and $v_i$ are used (see M2011 for details). For (semi-) volatile compounds, which can be driven out of the aerosol into the gas phase, an additional gas-aerosol interaction parameter (activity coefficient) is needed, which we determine similarly to the traditional activity coefficient, $\gamma_s$, through a parameterization given by Eq. (8) for single solute solutions, and Eq. (14) for mixed solutions, with the corresponding exponents given in Table 7 for NH$_4$NO$_3$ and NH$_4$Cl.

(h) Based on the AWC history, the liquid-solid partitioning is calculated using either the RHD or RHE values, whereby all compounds are assumed to be completely precipitated if the RH is below the compound $T$-dependent RHD or RHE value in case of single solute solutions. The salt compound is removed from the aqueous phase and assumed to be pure solid. In mixed solutions, a solid and liquid phase can co-exist in case compounds have different RHD or RHE values.

(i) For salt compounds present in a mixed solution, MRHD and MRHE values are applied; based on Eqs. (12) and (13), respectively. Optionally, the so-called mutual relative humidity of deliquescence (MRHD) values used in ISORROPIA II can be used, if the composition matches the same pre-defined aqueous salt compositions listed in Table 5 of Fountoukis and Nenes (2007); MRHE values are not available. EQSAM4 always applies the lowest RHD (or RHE) value of the compounds present in the solution, e.g. in case the MRHD (or MRHE) value is higher.

(j) The residual gases and acids (first row of Table 1 and NH$_3$) are computed from the remaining, i.e. non-neutralized “free” cations and anions. Phosphoric and sulfuric acid can optionally be assumed to remain in the aerosol phase, due to their very low vapor pressures.

(k) The aerosol liquid water content of single solutes (AWC) and mixed solutions (MAWC) is computed from Eqs. (9) and (11), respectively, for all selected compounds dissolved in the aqueous phase, i.e. when the RHD (or RHE) value is below the actual RH.

(l) The $H^+$ concentration and the pH of the solution is calculated from the MAWC, assuming electroneutrality and accounting for the auto-dissociation of water.

(m) The uptake of the gases (first row of Table 1 and NH$_3$) by aqueous solutions is parameterized using Eq. (14) and the corresponding coefficients given in Table 8.

(n) 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 or other reactions. However, they contribute to the aerosol mass, and as long as they remain hydrated also to
the aerosol water mass, and thus can effect the overall aerosol hygroscopic growth.

4. Diagnostic output calculations:

(a) Various aerosol properties can be stored for diagnostic purposes, such as the solution $pH = -\log \left( \sum_{j=1}^{l} (n_{s_j}/m_w) \right)$, and the ionic strength of binary and mixed solutions $Z = 0.5 \times (Z_{cs} + Z_{cs}) / m_w$, with $Z_{cs} = \sum_{j=1}^{l} z_{s_j}^c$ and $Z_{cs} = \sum_{j=1}^{l} z_{s_j}^s$ the total charge of cations and anions, respectively. Aerosol properties such as mass and number of moles, and the associated water mass are stored for each compound listed in Table 2 for each phase (gas, aqueous, solid). Additionally, the total particulate matter (PM), including solids and ions, can be expressed as the total number of moles, $PM = \sum_{j=1}^{l} n_{s_j}$, the total mass, $PM(t) = \sum_{j=1}^{l} n_{s_j} M_{s_j}$, and the total dry mass $PM_s(t) = \sum_{j=1}^{l} n_{s_j} M_{s_j}$, whereby mass and water fractions of all individual compounds are summed, optionally in different units (mol, µmol, or nmol).

3 Model applications

In this section we apply EQSAM4 to solve the gas-liquid-solid partitioning for various single solute and mixed solution modeling examples, including results of box model and global modeling applications. We focus on the RHD/RHE based water uptake of atmospheric aerosols, as this is a key process in atmospheric chemistry and climate modeling studies.

3.1 Box model comparison

We apply $\nu_i$ to solve the gas-liquid-solid partitioning with EQSAM4 using Eqs. (1–14). The results in this sub-section are all based on $\nu_i$ obtained from RHD measurements and compared to reference calculations of E-AIM and ISORROPIA II. For comparison, results based on $\nu_i$ estimated from Eq. (6) are included (label EQSAM4-Eq6).

3.1.1 Fixed solute concentrations: EQSAM4 vs. E-AIM and ISORROPIA II

Figure 4 present results of a box model inter-comparison using EQSAM4 and the thermodynamic reference model, E-AIM (Wexler and Clegg, 2002; http://www.aim.env.uea.ac.uk/aim/aim.php), and the thermodynamic model ISORROPIA II (Fountoukis and Nenes, 2007). ISORROPIA II is included in our global chemistry climate model EMAC (Pringle et al., 2010) – a comparison is given in the next section. The results in this section are based on the same RHD and MRHD values as used in ISORROPIA II, and the coefficients listed in Tables 7 and 8 have been applied to parameterize the mixed solution activity coefficient of volatile compounds with Eq. (14), i.e. NH$_4$NO$_3$, NH$_4$Cl, and the aqueous uptake of residual gases NH$_3$, HNO$_3$ and HCl.

Figure 4a–e shows box model results for the gas/liquid/solid aerosol equilibrium partitioning of various single salt solutions, and Fig. 4g–h shows the results of two corresponding mixed solutions. The solute concentrations were fixed to 1 [µmol/m$^3$]. The aerosol water and the RHD predicted by EQSAM4 compare relatively well with the predictions of E-AIM and ISORROPIA II for all salt solutions, although minor discrepancies occur. The main discrepancy between EQSAM4 and ISORROPIA II occurs at the phase transitions near the mutual RHD for the mixed solution case (h), which includes NH$_4$Cl, although the same MRHD values as used in ISORROPIA II have been applied for the mixed solution cases. The reason is that for this particular case ISORROPIA II does not predict NH$_4$Cl to be present in the mutual deliquescence RH regime, while it is the case for EQSAM4 and E-AIM. Near the upper end of the RH range, i.e. at high RH above 95 [%], the EQSAM4 aerosol water prediction starts to deviate from those
of E-AIM and ISORROPIA II, since the applied parameterization of solute molality, Eq. (7), becomes invalid. For cases with high RH values, the solute molality including the Kelvin-term should be used (see M2011). Nevertheless, the aerosol water uptake agrees well with the reference calculations, even if \( v_i \) is estimated from Eq. (6), except for case (f), i.e. \( \text{NH}_4\text{HSO}_4 \), where the simplified \( v_i \) estimation works less well. For compounds that do not dissociate completely, e.g. bi-sulfates (case (f)), this simplified estimation leads to relatively larger errors compared to compounds that practically dissociate completely, e.g. NaCl; i.e. comparing case (a) and (f). For a comprehensive model evaluation we refer to the revised publication of Xu et al. (2009, 2011), which complements this work. Next, we continue with mixed solution box modeling applications using observations following Metzger et al. (2006).

### 3.1.2 MINOS campaign: EQSAM4 vs. ISORROPIA II

To extend our model inter-comparison for mixed solutions, we apply EQSAM4 to real cases, i.e. measurements obtained from MINOS (Mediterranean INtensive Oxidant Study) in Crete in the period 27 July to 25 August 2001 following Metzger et al. (2006). For a general description of the measurements and the modeling set-up we refer to that article. Here, we compare EQSAM4 with ISORROPIA II and apply both models with the same level of complexity, considering the ammonium/sulfate/nitrate/chloride/sodium/calcium/magnesium/potassium/water system.

The EQSAM4 results in this section are based on the same RHD values as used in ISORROPIA II, while the MRHD values have been obtained from Eq. (12), and only the default cases with coefficients as in C0 of Table 7, i.e. \( x = 2 \) and \( x = 6 \) for the two volatile compounds, \( \text{NH}_4\text{NO}_3 \) and \( \text{NH}_4\text{Cl} \), respectively, have been applied to parameterize the mixed solution activity coefficient with Eq. (14) for all mixed solution cases (time steps, i.e. data points). The aqueous uptake of residual gases \( \text{NH}_3 \), \( \text{HNO}_3 \) and \( \text{HCl} \) is negligible since total aerosol liquid water content (AWC) is predicted to be rather low in the considered observation period, due the relatively high temperature and low relative humidity; \( T > 295\,[\text{K}] \) and \( \text{RH} < 90\,[\%] \), see panels (g) and (h) in Fig. 6 for \( T \) and RH, and respectively panels (a) in Figs. 5 and 6 for the total AWC of the aerosol fine and coarse mode. Figure 5 shows 4-weekly time series of model calculated mixed solution properties for the aerosol fine mode; observations are included where available. Figure 6 also shows the coarse mode results. The results of EQSAM4 and ISORROPIA II are close for all cases when \( v_i \) is determined from the compound's RHD. But even if \( v_i \) is estimated from Eq. (6) (labeled EQSAM4-Eq6) the results are rather close to ISORROPIA II. The relatively largest deviations occur for the aerosol water mass predictions and the liquid-solid partitioning.

Both models predict the same amounts of residual gases, \( \text{NH}_3 \), \( \text{HNO}_3 \) and \( \text{HCl} \) and a similar amount of the corresponding aerosol ammonium and nitrate in both the fine and coarse mode. Also the calculations of the low aerosol nitrate concentrations are similar, although quite sensitive to the activity coefficient of ammonium nitrate, but both models tend to overestimate the \( \text{NO}_3^- \) and \( \text{Cl}^- \) in the coarse mode compared to the observations, since the semi-volatile inorganic matter tends to be not in equilibrium. And the models do not necessarily need to be in agreement with ammonia and the observations of fine mode ammonium. The reason is that organic acids are omitted in this comparison because ISORROPIA II does not include them. Metzger et al. (2006) showed that the presence of ammonium in the aerosol phase could be 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, so that a consistent inclusion of alkaline cations and organic acids seems to be important for the gas/aerosol partitioning of reactive nitrogen compounds for both fine and coarse mode particles. In contrast to the cation ammonium, the anion nitrate is less affected in the fine mode than in the coarse mode, so that the aerosol nitrate predictions of EQSAM4 are closer to the observations for these cases.

### 3.2 Global model application with EMAC

To test the applicability of EQSAM4 in global modeling, we have applied EQSAM4 within our global chemistry climate model EMAC, with the setup exactly as in Pringle...
et al. (2010). We therefore refrain from further model description and refer instead to that article. Figures 7 and 8 complement their Figs. 14 and 15, showing the same results for EQSAM4 instead for ISORROPIA II (both gas-aerosol partitioning models are embedded within EMAC/GMXe and applied exactly the same). Figure 7 compares the EQSAM4 based results with data collected by AEROCE. Maps show the surface concentration of nitrate (top) and sulfate (bottom) for the year 2002; the observations are overplotted (squares). Scatter plots show the comparison of the EQSAM4 model vs. AEROCE data for nitrate (top) and sulfate (bottom). Figure 8 (top) additionally shows the annual mean AOD modeled with GMXe/EQSAM4 for the year 2001; over-plotted are annual mean measurements from the AERONET network (2001), and a summary of the comparison between GMXe using EQSAM4 and AERONET is given in the left bottom panel, while the right bottom panel shows the annual mean AOD from MODIS for the year 2001. Both figures are similar to the ISORROPIA II based ones shown in Pringle et al. (2010). We only include these results for the purpose of a consistent model inter-comparison between EQSAM4 and ISORROPIA II within EMAC. For a comprehensive AOD evaluation a coupling of the gas-aerosol partitioning module (here EQSAM4 or ISORROPIA II) with the module that calculates the size-dependent aerosol dynamics (GMXe), following e.g. Feng and Penner (2007), is required. A further development is foreseen.

4 Conclusions

Version 4 of the EQuilibrium Simplified Aerosol Model (EQSAM4), which is part of our aerosol chemistry-microphysics module (GMXe) and chemistry-climate model (EMAC), is described and evaluated. We focus on the RHD based water uptake of atmospheric aerosols, e.g. important for calculations of the aerosol optical depth (AOD). The key equations on which EQSAM4 builds are detailed in M2011 (companion paper) and based on a solute specific coefficient \( \nu \). To demonstrate the applicability of EQSAM4, we have given some examples; starting from computations based on the key equations, to box and global modeling. It appears that the \( \nu \) concept can be applied to solve the gas-liquid-solid partitioning of single solute or mixed solutions and thus the RHD/RHE based water uptake of atmospheric aerosols. The results of EQSAM4 closely agree with the results of the thermodynamic reference model E-AIM and also with ISORROPIA II for various single and mixed salt solutions. A more comprehensive box-model comparison is the subject of a revised publication (Xu et al., 2009, 2011). Our box model results are supported by global modeling applications and a comparison with measurements and with results of ISORROPIA II, as presented earlier following Pringle et al. (2010). Our results indicate that the revised EQSAM model provides a valid parameterization for global modeling.

Acknowledgements. This work was supported by the CIRCE Integrated Project – Climate Change and Impact Research: the Mediterranean Environment (http://www.circeproject.eu/) and supported by the European Commission’s Sixth Framework Program, Sustainable Development, Global Change and Ecosystems, Project No. 036961. We are grateful to the ERC for support of the C8 project. LX and JEP are grateful for the support of the NASA Glory Science Team under grant number NNX08AL83G as well as that from NASA JPL under contract number NM0710973. LX is grateful for the support for the Max Planck Society. We thank T. Nenes for kindly providing the ISORROPIA II source code and S. L. Clegg and A. S. Wexler for the www version of E-AIM. We thank K. Pringle and H. Tost for their support with the ongoing model development of EQSAM/GMXe.

References


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Table 1a. EQSAM4 compounds and data.

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**Note:**
- m̂: molar mass [g/mol]
- s: solubility, mass percent [%] (of dry mass)
- m̂: molar density [g/g]
- s: solubility, mass percent [%] (of dry mass)
- m̂: molar density [g/g]

**References:**
Table 1c. Continued.

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<td>0.30</td>
<td>58.32</td>
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<td>1.7954</td>
<td>47.26</td>
<td>1.04</td>
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<tr>
<td></td>
<td>1.25</td>
<td>47.26</td>
<td>1.00</td>
<td>2826</td>
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</tbody>
</table>
Table 2. RHD values at $T_o$ and the $T$-coefficients for major salt compounds used to determine $\nu_i$.

<table>
<thead>
<tr>
<th>Solute</th>
<th>NaCl</th>
<th>NaNO$_3$</th>
<th>Na$_2$SO$_4$</th>
<th>NH$_4$NO$_3$</th>
<th>(NH$_4$)$_2$SO$_4$</th>
<th>NH$_3$HSO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>RHD($T_o$)</td>
<td>0.7528</td>
<td>0.7379</td>
<td>0.930</td>
<td>0.6183</td>
<td>0.7997</td>
<td>0.400</td>
</tr>
<tr>
<td>$T$-coefficient</td>
<td>25.00</td>
<td>304.00</td>
<td>80.00</td>
<td>852.00</td>
<td>80.00</td>
<td>384.00</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Solute</th>
<th>(NH$_4$)$_2$(HSO$_3$)$_2$</th>
<th>NH$_4$Cl</th>
<th>NaHSO$_3$</th>
<th>Ca(NO$_3$)$_2$</th>
<th>CaCl$_2$</th>
<th>K$_2$SO$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>RHD($T_o$)</td>
<td>0.6900</td>
<td>0.7710</td>
<td>0.520</td>
<td>0.4906</td>
<td>0.2830</td>
<td>0.9750</td>
</tr>
<tr>
<td>$T$-coefficient</td>
<td>186.00</td>
<td>239.00</td>
<td>-45.00</td>
<td>509.40</td>
<td>551.10</td>
<td>35.60</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Solute</th>
<th>KHSO$_4$</th>
<th>KNO$_3$</th>
<th>KCl</th>
<th>MgSO$_4$</th>
<th>Mg(NO$_3$)$_2$</th>
<th>MgCl$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>RHD($T_o$)</td>
<td>0.860</td>
<td>0.9246</td>
<td>0.8426</td>
<td>0.8613</td>
<td>0.5400</td>
<td>0.3284</td>
</tr>
<tr>
<td>$T$-coefficient</td>
<td>0.000</td>
<td>0.000</td>
<td>159.00</td>
<td>-714.45</td>
<td>230.20</td>
<td>42.23</td>
</tr>
</tbody>
</table>

Table 3. Relative humidity of deliquescence (RHD) at $T^o = 298$ [K]. Bold values represent measurements, non-bold values are obtained from Eqs. (3) and (1). All non-bold values are indicative (measurements are required for validation).

| Solute | PO$_4$ | SO$_4$ | HSO$_4$ | NO$_3$ | Cl | Br | I | Cl$^2$ | HCO$_3$ | OH | NH$_3$ | NH$_2$ | N$_2$ | N$_2$ | N$_2$ | N$_2$ | N$_2$ | N$_2$ | N$_2$ | N$_2$ | N$_2$ | N$_2$ | N$_2$ |
|--------|--------|--------|---------|--------|----|----|---|--------|---------|----|-------|-------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| Na$_2$ | 0.9321 | 0.7307 | 0.4081 | 0.8156 | 0.7711 | 0.7727 | 0.7468 | 0.7390 | 0.9469 | 0.9300 | 0.5827 | 0.6327 | 0.5485 | 0.6083 | 0.5989 | 0.5989 | 0.5989 | 0.5989 | 0.5989 | 0.5989 | 0.5989 | 0.5989 |
| Na$_2$ | 0.9064 | 0.93 | 0.52 | 0.738 | 0.7626 | 0.7683 | 0.7488 | 0.7878 | 0.9604 | 0.5102 | 0.6842 | 0.7851 | 0.6642 | 0.5089 | 0.5989 | 0.5989 | 0.5989 | 0.5989 | 0.5989 | 0.5989 | 0.5989 | 0.5989 |
| Na$_2$ | 0.8661 | 0.975 | 0.06 | 0.8246 | 0.8447 | 0.8243 | 0.7952 | 0.8790 | 0.5779 | 0.5133 | 0.5869 | 0.9182 | 0.4930 |
| Ca$^{2+}$ | 0.7459 | 0.457 | 0.0054 | 0.457 | 0.2323 | 0.0223 | 0.8423 | 0.0284 | 0.8389 | 0.0430 | 0.0849 | 0.9288 | 0.6083 |
| Mg$^{2+}$ | 0.4233 | 0.8861 | 0.5401 | 0.3286 | 0.8511 | 0.8705 | 0.6742 | 0.8742 | 0.4939 | 0.4852 | 0.4170 |
| Fe$^{3+}$ | 0.6373 | 0.8301 | 0.0907 | 0.8436 | 0.7429 | 0.8868 | 0.0249 | 0.7745 | 0.0249 | 0.4852 |

Table 4. Relative humidity of efflorescence (RHE) at $T = 298$ [K] and obtained with Eq. (2). All values are indicative (measurements are required for validation).

Table 5. Mixed solution domains (D1–10) to identify certain regimes, applied to determine $x$ in Eq. (14).
Table 6. Mixed solution regimes (R1–6) that apply to each of the 10 domains listed in Table 5. X and Y either refer to the total of cations or anions, depending on the domain listed in Table 5.

<table>
<thead>
<tr>
<th>Regime</th>
<th>Regime X to Y threshold classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>$t_X / t_Y &gt; 2$ X very rich</td>
</tr>
<tr>
<td>R2</td>
<td>$t_X / t_Y &gt; 1$ X rich</td>
</tr>
<tr>
<td>R3</td>
<td>$t_X / t_Y \leq</td>
</tr>
<tr>
<td>R4</td>
<td>$t_X / t_Y &lt; -1$ X poor</td>
</tr>
<tr>
<td>R5</td>
<td>$t_X / t_Y &lt; -2$ X very poor</td>
</tr>
<tr>
<td>R6</td>
<td>$t_X / t_Y \leq -3$ no X</td>
</tr>
</tbody>
</table>

Table 7. Solution cases that identify combinations of concentration regimes according to Tables 5 and 6. The cases specify the activity coefficient exponent $x$ for the two volatile salt compounds, i.e. $\text{NH}_4\text{NO}_3$ and $\text{NH}_4\text{Cl}$ in mixed solutions (for the other salt compounds of Table 1 no cases are applied). Note that the following definitions refer to Table 6: sulfate very rich equals R5; sulfate rich, R4; sulfate neutral, R3; sulfate poor, R2; sulfate very poor, R1. Pure compound refers to a single solute solution.

<table>
<thead>
<tr>
<th>Domain</th>
<th>D8</th>
<th>D10</th>
<th>D7</th>
<th>D6</th>
<th>D4</th>
<th>D5</th>
<th>$x_{\text{NH}_4\text{NO}_3}$</th>
<th>$x_{\text{NH}_4\text{Cl}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.00</td>
<td>2.00</td>
</tr>
<tr>
<td>C1–5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.00</td>
<td>2.00</td>
</tr>
<tr>
<td>C6–10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.00</td>
<td>2.00</td>
</tr>
<tr>
<td>C10</td>
<td>R4</td>
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<td>R5</td>
<td>R5</td>
<td>R5</td>
<td>R5</td>
<td>0.00</td>
<td>0.50</td>
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<tr>
<td>C10–20</td>
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<td></td>
<td>2.00</td>
<td>2.00</td>
</tr>
<tr>
<td>C11</td>
<td>R2</td>
<td>R4</td>
<td>R6</td>
<td>R6</td>
<td>R6</td>
<td>R6</td>
<td>0.00</td>
<td>0.50</td>
</tr>
<tr>
<td>C12</td>
<td>R2</td>
<td>R2</td>
<td>R6</td>
<td>R6</td>
<td>R6</td>
<td>R6</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>C13</td>
<td>R4</td>
<td>R4</td>
<td>R5</td>
<td>R6</td>
<td>R6</td>
<td>R6</td>
<td>0.00</td>
<td>1.00</td>
</tr>
<tr>
<td>C14</td>
<td>R2</td>
<td>R4</td>
<td>R5</td>
<td>R6</td>
<td>R6</td>
<td>R6</td>
<td>0.00</td>
<td>0.25</td>
</tr>
<tr>
<td>C15</td>
<td>R2</td>
<td>R4</td>
<td>R2</td>
<td>R6</td>
<td>R6</td>
<td>R6</td>
<td>1.00</td>
<td>0.125</td>
</tr>
<tr>
<td>C16</td>
<td>R4</td>
<td>R4</td>
<td>R5</td>
<td>R5</td>
<td>R5</td>
<td>R5</td>
<td>0.00</td>
<td>1.00</td>
</tr>
<tr>
<td>C17</td>
<td>R2</td>
<td>R4</td>
<td>R5</td>
<td>R5</td>
<td>R5</td>
<td>R5</td>
<td>2.00</td>
<td>0.25</td>
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<tr>
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<td>R2</td>
<td>R4</td>
<td>R5</td>
<td>R5</td>
<td>R5</td>
<td>R5</td>
<td>1.00</td>
<td>0.125</td>
</tr>
<tr>
<td>C19</td>
<td>R2</td>
<td>R4</td>
<td>R5</td>
<td>R5</td>
<td>R5</td>
<td>R5</td>
<td>2.00</td>
<td>0.25</td>
</tr>
<tr>
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<td>R2</td>
<td>R2</td>
<td>R6</td>
<td>R5</td>
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<td>R5</td>
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<td>2.00</td>
</tr>
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<td>C21</td>
<td>R3</td>
<td>R6</td>
<td>R4</td>
<td>R6</td>
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<td>R6</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>C22</td>
<td>R2</td>
<td>R4</td>
<td>R4</td>
<td>R6</td>
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<td>R6</td>
<td>0.25</td>
<td>0.25</td>
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<tr>
<td>C23</td>
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<td></td>
<td></td>
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<td>0.25</td>
<td>0.25</td>
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</table>
Table 8. Same as Table 6 but applied for the uptake of gases in aqueous solutions, i.e. all compounds in the first row of Table 1 and NH\(_3\) (first compound in last row), with \(x\) and \(y\) in Eq. (14).

<table>
<thead>
<tr>
<th>Domain</th>
<th>D8</th>
<th>D10</th>
<th>D7</th>
<th>D6</th>
<th>D4</th>
<th>D5</th>
<th>(x_{\text{gases}})</th>
<th>Domain</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case</td>
<td>NH(_3^+) NO(_3^-) Na(^+) K(^+) Ca(^{2+}) Mg(^{2+}) (y)</td>
<td>(x)</td>
<td>specification</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C0</td>
<td>sulfate very rich</td>
<td>0.075</td>
<td>8.00</td>
<td>D2</td>
<td>(&lt; 1.0)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C1–5</td>
<td>sulfate rich</td>
<td>0.25</td>
<td>2.00</td>
<td>D2</td>
<td>(&lt; 2.0)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C6–10</td>
<td>sulfate neutral</td>
<td>0.50</td>
<td>2.00</td>
<td>D2</td>
<td>(&lt; 2.0)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C11–23</td>
<td>sulfate poor</td>
<td>0.50</td>
<td>2.00</td>
<td>D2</td>
<td>(\geq 2.0)</td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>

Fig. 1a. Single solute molality as a function of water activity for several electrolytes: (NH\(_4\))\(_2\)SO\(_4\), Na\(_2\)SO\(_4\), NH\(_4\)Cl, NaCl (at \(T = 298.15\) K) calculated with EQSAM4 from Eq. (1) and compared to tabulated data used in ISORROPIA II and EQUISOLV II.
Fig. 1b. Same as Fig. 1a for (NH₄)HSO₄, NaHSO₄, NH₄NO₃, NaNO₃ (at T = 298.15 K).

Fig. 2. Binary activity coefficient of NH₄NO₃ and NH₄Cl at T = 298 K; obtained for EQSAM4 as a function of solute molality and RH with Eq. (8). The values used by ISORROPIA II (Fountoukis and Nenes, 2007) and EQUISOLV II (Jacobson, 1999) are included for comparison.
1. Model initialization:
Reading input gas/aerosol input concentrations, T, RH; definition of switches and selection of compounds.

2. Pre-calculation of look-up tables:
Calculation of the T-dependency of the RHD and solubility (\(w_s\)) measurements;
Determination of the solute specific coefficient \(v_s\) from the T-dependent \(w_s\) and RHD data, and from Eq. (6);
(Re-)calculation of the RHD(T) and RHE(T) values for all compounds with Eq. (1) and (2) using \(w_s(T)\) and \(v(T)\);
In case the Kelvin-term is considered, the solute molality \(\mu_s\) is pre-calculated for the upper RH range, 0.98<RH<1.1.

3. Runtime calculations - gas/liquid/solid aerosol equilibrium partitioning:
RH-dependent solute properties are calculated during runtime for a given RH and T;
The neutralization reactions are solved and salt compounds are calculated from the neutralization of input cation and anion concentrations, with the reaction order either determined automatically, or prescribed (and T-independent), with a special treatment of bi-salts and volatile salts;
Based on the AWC history, the liquid-solid partitioning is calculated using either the RHD or RHE values;
for salt compounds present in a mixed solution, MRHD and MRHE values are applied.
Gas/liquid partitioning is calculated for all volatile compounds and the total aerosol liquid water content (AWC) from all single solutes.
The pH of the solution is calculated from the AWC, and the uptake of the residual gases by aqueous solutions.
Non-electrolyte solutes not directly considered for the neutralization reactions, but they contribute to the aerosol mass, and as long as they remain hydrated also to the AWC.

4. Diagnostic output calculations:
Various aerosol properties can be stored for diagnostic purposes: e.g. pH, ionic strength, aerosol liquid water content, aqueous and dry particulate matter (PM), total PM, mass and number of moles of each compound in gas, liquid, solid aerosol phase, masses can be given different units: mol, \(\mu\)mol, or nmol.

Fig. 3. Generic solution procedure of EQSAM4.

Fig. 4a–d. Water uptake of atmospheric aerosols – single salt solutions fixed to 1 [\(\mu\)mol(solute)/m\(^3\)(air)]: (a, c) NaCl–H\(_2\)O and (b, d) (NH\(_4\))\(_2\)SO\(_4\)–H\(_2\)O, with (a, b) RH ≤95 [%] and (c, d) RH ≥95 [%], showing EQSAM4 (red crosses) versus E-AIM (web version) (blue circles) and ISORROPIA II (green squares).
Fig. 4e–h. Continued. Single salt solutions of (e) NH₄NO₃–H₂O and (f) NH₄HSO₄–H₂O, and corresponding mixed solutions of (g) NaNO₃–NaCl–H₂O and (h) (NH₄)₂SO₄–NH₄Cl–Na₂SO₄–H₂O. All single solute concentrations were fixed to 1 [µmol/m³(air)], and the same MRHD values as used in ISORROPIA II have been applied for the mixed solution cases.

Fig. 5a–d. MINOS Campaign. Aerosol fine mode. Mixed solution properties and model comparison, following Metzger et al. (2006). (a) Aerosol water mass [µg/m³(air)], (b) total particulate matter (PM) [µg/m³(air)], (c) total solid matter (PM) [µg/m³(air)], (d) total number of moles of (PM) [µmol/m³(air)]. All panels show time series for the period 28 July–25 August 2001 and show the EQSAM4 results based on ν, determined from the compound RHD (red crosses), EQSAM4-Eq6 based on ν, estimated from Eq. (6) (turquoise triangles), ISORROPIA II (green open squares). Measurements are included, if available (blue open circles).
Fig. 5e–h. Continued. (e) total particulate ammonium, (f) total particulate sodium, (g) total particulate potassium, (h) total particulate calcium. All concentration are in [nmol/m\(^3\) (air)].

Fig. 5i–l. Continued. (i) total particulate magnesium, (j) total particulate sulfate, (k) total particulate bi-sulfate, (l) total particulate nitrate. All concentration are in [nmol/m\(^3\) (air)].
Fig. 5m–p. Continued. (m) total particulate chloride, (n) residual gaseous HCl, (o) residual gaseous HNO$_3$, (p) residual gaseous NH$_3$. All concentration are in [nmol/m$^3$(air)].

Fig. 6a–d. As Fig. 5 with results for the aerosol coarse mode. (a) Aerosol water mass [µg/m$^3$(air)], (b) total particulate matter (PM) [µg/m$^3$(air)], (c) total solid matter (PM) [µg/m$^3$(air)], (d) total number of moles of (PM) [µmol/m$^3$(air)].
Fig. 6e–h. Continued. (e) total particulate nitrate [nmol/m³(air)], (f) particulate chloride [nmol/m³(air)], (g) observed temperature [°C], (h) observed relative humidity [%].

Fig. 7. Comparison of model results to data collected in AEROCE. Maps show surface concentrations of nitrate (top) and sulfate (bottom) for the year 2002 simulated using EQSAM4. The over-platted squares represent data from AEROCE. Scatter plots show the comparison of model vs. AEROCE data for nitrate (top) and sulfate (bottom); observations are included for the year 2001 (triangles) and 2002 (stars). Units are [µg/m³(air)].
Fig. 8. (Top) Annual mean AOD modeled with GMXe for the year 2001; over-plotted are annual mean measurements from the AERONET network (2001). (Bottom left) Summary of the comparison between GMXe using EQSAM4 and AERONET, black crosses are monthly means and red annual means ($r^2 = 0.51$). (Bottom right) Annual mean AOD from MODIS for the year 2001. Figures 7 and 8 complement Figs. 14 and 15 of Pringle et al. (2010).