Gas/aerosol partitioning:
1. A computationally efficient model

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[1] A computationally efficient model to calculate gas/aerosol partitioning of semivolatile inorganic aerosol components has been developed for use in global atmospheric chemistry and climate models. We introduce an approximate method for the activity coefficient calculation that directly relates aerosol activity coefficients to the ambient relative humidity, assuming chemical equilibrium. We demonstrate that this method provides an alternative for the computationally expensive iterative activity coefficient calculation methods presently used in thermodynamic gas/aerosol models. The gain of our method is that the entire system of the gas/aerosol equilibrium partitioning can be solved noniteratively, a substantial advantage in global modeling. We show that our equilibrium simplified aerosol model (EQSAM) yields results similar to those of current state-of-the-art equilibrium models.

INDEX TERMS: 1610 Global Change: Atmosphere (0315, 0325); 5704 Planetology: Fluid Planets: Atmospheres—composition and chemistry; 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); KEYWORDS: inorganic aerosols, aerosol composition, aerosol water, thermodynamic equilibrium, gas/aerosol partitioning parameterization

1. Introduction

[2] Atmospheric aerosols are usually mixtures of many components, partly composed of inorganic acids (e.g., H2SO4, HNO3), their salts (e.g., (NH4)2SO4, NH4NO3), and water [e.g., Charlson et al., 1978; Heintzenberg, 1989]. Because many compounds are highly hygroscopic, aerosol associated water often exceeds the dry aerosol mass [e.g., Pilinis et al., 1989], especially in the humid lower troposphere. Both the dry aerosol mass and the aerosol associated water are important in climate change scenario simulations [e.g., Charlson et al., 1987; Charlson and Wigley, 1994; Charlson and Heintzenberg, 1995; Pilinis et al., 1995; Intergovernmental Panel on Climate Change (IPCC), 1996]. Nevertheless, multicomponent aerosol concentrations are not yet routinely calculated within global atmospheric chemistry or climate models. The reason is that simulations of these aerosol particles, especially those including semivolatile components, require complex and computationally expensive thermodynamic calculations. For instance, the aerosol-associated water depends on the composition of the particles, which is determined by the gas/liquid/solid partitioning, which is in turn strongly dependent on temperature and relative humidity.

[3] In the past two decades much effort has been devoted to the development of methods for the calculation of aerosol properties that are difficult to measure. These properties include the aerosol phase composition (i.e., solid or liquid) and the aerosol-associated water mass. Most attention has focused on the inorganic aerosol compounds that are often predominant, such as sulfate, ammonium, nitrate and aerosol water. These compounds partition between the liquid-solid aerosol phases and the gas phase of aerosol precursor gases such as HNO3 and NH3. Therefore numerous thermodynamic models have been developed [Bassett and Seinfeld, 1983, 1984; Saxena et al., 1986; Binkowski, 1991; Pilinis and Seinfeld, 1987; Wexler and Seinfeld, 1991; Kim et al., 1993a, 1993b; Kim and Seinfeld, 1995; Meng and Seinfeld, 1996; Nenes et al., 1998; Clegg et al., 1998a, 1998b; Jacobson et al., 1996; Jacobson, 1999], and several gas/aerosol dynamic models [Meng et al., 1998; Sun and Wexler, 1998; Pilinis et al., 2000]. While the first generation models, to which we refer in the following as equilibrium models (EQMs), assumed thermodynamic equilibrium between the gas/liquid/solid aerosol phases, neglecting mass transfer between the liquid/solid aerosol phases and the gas phase, the second generation dynamical models calculate mass transfer explicitly, e.g., by incorporating an EQM [Pilinis et al., 2000]. For a comparative review, see Zhang et al. [1999a, 1999b].

[4] Most of these models were developed for incorporation into urban and regional scale air quality models. Numerical EQM schemes generally solve the system of nonlinear gas/aerosol equilibrium equations using different types of iterative schemes. The number of iterations needed to solve the equilibrium equations strongly depends on the aerosol composition and the meteorological conditions. For instance, if some aerosol compounds are predicted to be solid, additional iterations are needed to calculate both the liquid-solid phase transitions, and the partitioning between liquid/solid aerosol phases and the gas phase. Even in the relatively simple case of pure aqueous phase particles, the
composition is calculated iteratively. The reason is that common calculation methods of the aerosol composition need information about the solute activity, which includes the aerosol-associated water, and which determines the vapor pressure above the aerosol.

[5] To reduce the computational costs of the gas/aerosol partitioning calculations, different approaches have been proposed as an alternative to the iterative calculations. These include the use of neural networks [Potukuchi and Wesler, 1997] to obtain the equilibrium partial pressures of the semivolatile aerosol components, the use of pre-calculated sets of activity coefficients which are the crucial part of the iteration procedure in an EQM (ISORROPIA, see Nenes et al. [1998]), and polynomial fits of pre-calculated activity coefficients [Metzger et al., 1999]. However, if incorporated into a global model, even the optimized EQM ISORROPIA accounts for most of the total computational burden [Adams et al., 1999, 2001]. Therefore, we have developed a computationally efficient gas/aerosol partitioning model specifically for global modeling (EQSAM: Equilibrium Simplified Aerosol Model). The approach used for EQSAM is based on the relationship between activity coefficients and the relative humidity [Metzger et al., 1999]. This relationship allows parameterization of the relevant nonideal solution properties, which is sufficiently accurate for global modeling [Metzger, 2000]. Although EQSAM is solely based on parameterizations, the thermodynamic framework is based on the same assumptions used by other EQMs; for a more detailed discussion, we refer to Metzger [2000] (available at http://www.library.uu.nl/digiarchief/dip/diss/1930853/inhoud.htm).

[6] For a general discussion of the aerosol thermodynamics and the EQMs, we refer to Denbigh [1981], Seinfeld and Pandis [1998], Wesler and Potukuchi [1998], and the references therein; for a discussion of the interaction of aerosols with clouds, see, e.g., Pruppacher and Klett [1997].

[7] EQSAM is introduced in section 2. In section 3, EQSAM is evaluated against other thermodynamic models presently in use in urban and regional chemical transport models. This model comparison includes box-model calculations and global offline calculations, as well as online calculations. For the latter part, EQSAM and the state-of-the-art EQM ISORROPIA will be applied to global atmospheric chemistry modeling, with both routines fully coupled to an atmospheric chemistry-transport model. The results will be discussed in section 4. We extend the online model study in the accompanying paper of Metzger et al. [2002] (hereinafter referred to as M2002) to investigate and discuss the gas/aerosol partitioning on a global scale (using EQSAM). There, we also focus on the relevance of the gas/aerosol partitioning for global modeling, and on the estimation of the associated uncertainties, including a comparison with ground-based measurements.

2. Model Description

[8] The basic concept of EQSAM is that the activities of atmospheric aerosols in equilibrium with the ambient air are governed by the relative humidity (RH). Since the water activity is fixed by RH, the solute activity is, for a given aerosol composition, a function of RH; the molality depends on the water mass, which solely depends on RH (for a given solute). This is also approximately true for activity coefficients of salt solutes of binary and multicomponent solutions. The latter is a direct consequence of the ZSR-relation (see section 2.1). Consequently, activity coefficients can be directly derived from specific functions (see section 2.5). Using the “domain structure” (see section 2.2), and taking into account that gas/aerosol equilibrium is only valid for certain domains where sulfate is completely neutralized, we can noniteratively calculate the aerosol composition, including aerosol-associated water. A schematic description of EQSAM is given in Figure 1; the most important aspects will be discussed in the following.

2.1. General Assumptions

[9] The main assumptions basic to EQSAM, as to other EQMs, are that aerosols are internally mixed and obey thermodynamic gas/aerosol equilibrium. Both assumptions are expected to be accurate under most atmospheric conditions considering the time steps used by global chemical transport models. For instance, Meng and Seinfeld [1996] have shown that the time required for gas/aerosol equilibration depends primarily on the aerosol size and less on the temperature; small particles have a larger surface-to-volume ratio, therefore equilibrating faster than larger ones. In addition, the equilibration times of relevant aerosol species have been shown to be of the order of minutes [Khlystov, 1998; Dassios and Pandis, 1999]. These timescales are much shorter than the time steps of global atmosphere/chemistry models calculating chemistry and transport processes (typically 0.5–2 hours). The equilibrium approach can therefore be assumed adequate for global modeling.

[10] The equilibrium assumption further implies that the water activity (aw) of an aqueous aerosol particle is equal to the ambient relative humidity (RH), i.e., aw = RH; RH defined on the fraction scale [0–1] [Bassett and Seinfeld, 1983]. This is valid for atmospheric applications, since the ambient relative humidity is not influenced by the small water uptake of aerosol particles. From aw = RH it follows that the aerosol molality of a single solute or a mixture of solutes changes with ambient relative humidity. To obtain the molality of a mixture of solutes, the total water content of the aerosols is calculated in EQMs based upon a mixing rule that is widely used in atmospheric aerosol modeling, i.e., the so-called ZSR-relation named after Zdanovskii [1948] and Stokes and Robinson [1966]. This semiempirical relation simply assumes that a mixture of single-solute solutions has the same water activity as each single-solute solution, because aw = RH [Chen et al., 1973]. The ZSR-relation has been shown to be an excellent approximation for most atmospheric applications [Cohen et al., 1987a, 1987b; Kim et al., 1993b].

2.2. Concentration Domains

[11] To increase the computational efficiency of EQSAM the total number of equilibrium reactions is minimized by making use of concentration domains, as described by Nenes et al. [1998]. Each of these domains contains fewer species than the entire set of possible aerosol compositions. The domains are based on additional assumptions: Because sulfuric acid has a very low vapor pressure, it is assumed
1. **Concentration Domains**

<table>
<thead>
<tr>
<th>Domain number</th>
<th>Ratio</th>
<th>Domain</th>
<th>Sulfate state</th>
</tr>
</thead>
<tbody>
<tr>
<td>N=2</td>
<td>tNH₃ &gt; 2 tSO₄</td>
<td>⇒ sulfate neutral</td>
<td>Γ=2.0</td>
</tr>
<tr>
<td>N=3</td>
<td>tNH₃ &lt; 2 tSO₄</td>
<td>⇒ sulfate rich</td>
<td>Γ=1.5</td>
</tr>
<tr>
<td>N=4</td>
<td>tNH₃ &lt; 2 tSO₄</td>
<td>⇒ sulfate very rich</td>
<td>Γ=1.0</td>
</tr>
</tbody>
</table>

Free ammonia: \( \text{NH}_3^+ = t\text{NH}_3 - \Gamma \cdot t\text{SO}_4 \)

\( t\text{NH}_3 \) denotes \( \text{NH}_3+\text{NH}_4^+ \) and \( t\text{SO}_4=\text{H}_2\text{SO}_4+\text{SO}_4^{2-} \)

2. **Subdomains**

- e.g. Domain \( N=2 \) (sulfate neutral/poor): ⇒ gas/aerosol partitioning

(subdomains include various RHDs for single salts and MDRHs for mixed salts)

\( \text{RH} < \text{RHD}(T)_{\text{NH}_3\text{NO}_3} \quad \Rightarrow \text{gas-solid equilibrium} \)

\( \text{RH} > \text{RHD}(T)_{\text{NH}_3\text{NO}_3} \quad \Rightarrow \text{gas-liquid equilibrium} \)

3. **Equilibrium Constant**

\( K_{\text{NH}_3\text{NO}_3} = \gamma_{\text{NH}_3\text{NO}_3}^2 \left[ \text{NH}_3\text{NO}_3 \right] \left[ \text{NH}_4^+ \right]^i \left[ \text{HNO}_3 \right]^i \)

\( \Rightarrow \text{NO}_3^{i}_{\text{aq}} = f(T) \quad \Rightarrow \text{NO}_3^{i}_{\text{aq}} = f(T,\text{RH}) \)

4. **Activity Coefficients**

\( \gamma_{\text{NH}_3\text{NO}_3} = 1 \quad \quad \gamma_{\text{NH}_3\text{NO}_3} = \left[ \frac{\text{RH}^T}{(1000/N \cdot (1-\text{RH}) + N)} \right]^{1/8} \)

5. **Single Solute (ss) Molalities**

\( m_{\text{ss}} = (1000 \cdot f \cdot \gamma^i_{\text{ss}} \cdot (1/rh - 1)/M_j)^i \)

6. **Aerosol Concentrations**

\( \text{HNO}_3 = t\text{HNO}_3 - \text{NO}_3^+ \)

\( \text{NH}_3 = t\text{NH}_3 - \text{NH}_4^+ \)

\( \text{H}_2\text{SO}_4 = t\text{SO}_4 - \Gamma \cdot (t\text{NH}_3 - \text{NH}_3^+) \)

\( \text{NH}_4^{+}_{\text{aq}} = t\text{NH}_4^+ \cdot \text{NH}_3 \)

\( \text{SO}_4^{2-}_{\text{aq}} = t\text{SO}_4 \cdot \text{H}_2\text{SO}_4 \)

\( \text{PM}_{0+} = 62 \cdot \text{NO}_3^{i}_{\text{aq}} + 18 \cdot \text{NH}_4^{+}_{\text{aq}} + 96 \cdot \text{SO}_4^{2-}_{\text{aq}} \)

\( \text{PM}_{4+} = 62 \cdot \text{NO}_3^{i}_{\text{aq}} + 18 \cdot \text{NH}_4^{+}_{\text{aq}} + 96 \cdot \text{SO}_4^{2-}_{\text{aq}} \)

\( \text{tPM} = \text{PM}_{0+} + \text{PM}_{4+} \)

7. **Aerosol Water (W), Aerosol Radius Increase (r_a)**

\( W = \frac{\text{NH}_4\text{NO}_3}{m_{\text{ss}\text{NH}_4\text{NO}_3}} + (\text{NH}_3)^2\text{SO}_4/m_{\text{ss}(\text{NH}_3)^2\text{SO}_4} + \)

\( \text{NH}_4\text{H}_2\text{SO}_4/m_{\text{ss}\text{NH}_4\text{H}_2\text{SO}_4} + \ldots + \text{H}_2\text{SO}_4/m_{\text{ss}\text{H}_2\text{SO}_4} \)

\( r_a = 1 \quad \quad r_a = (W / (\text{PM} + 1))^{1/3} \)

**Figure 1.** Sequential overview of the Eeqsam structure. Note that the parameterizations in row 5 are discussed by Metzger [2000]. The parameters are given in Table 2; \( f = 0.81 \) for all species.
that it resides completely in the aerosol phase. Depending on mole ratios of the input concentrations (expressed in molar units) of, e.g., total ammonium to sulfate, sulfate is neutralized either completely or partially, so that each domain represents a certain aerosol type (total denotes the sum of the gas and aerosol concentration). In EQSAM currently 3 main domains are used (Figure 1, point 1; the prefix \( t \) denotes total).

[12] The subdivision of the input concentration into concentration domains according to the mole ratios thus yields the number of reactions, order and domain specific parameterizations (see section 2.5). Additionally, each concentration domain is further divided into several subdomains, according to the regime of deliquescence relative humidity of the corresponding salt compound.

2.3. Relative Humidity of Deliquescence

[13] Whether gas/aerosol equilibrium is calculated between the gas phase and a pure solid, or ions in an aqueous solution, depends on the deliquescence behavior of the considered aerosol compound. Certain salts, such as ammonium sulfate or ammonium nitrate, deliquesce if the relative humidity reaches a threshold value; below that these salts may be crystalline. However, certain aerosol mixtures (e.g., solutions containing sulfuric acid) do not deliquesce; rather they remain aqueous regardless the ambient relative humidity. As in most EQMs, the deliquescence of various salt compounds is determined in EQSAM in the corresponding subdomains. The deliquescence of salt aerosols depends on the ambient RH and temperature. The deliquescence behavior has been investigated for single salt solutions by, for instance, Wexler and Seinfeld [1991], and for multiple-salt solutions by, e.g., Tang and Munkelwitz [1993].

[14] For modest atmospheric temperature variations, \( T - T_0 \), with \( T \) the ambient temperature and \( T_0 \) the standard temperature, the relative humidity of deliquescence (RHD) and the mutual deliquescence relative humidity (MDRH) of multicomponent salt particles can be expressed as [Nenes et al., 1998]

\[
\ln[\text{MDRH}(T)/\text{MDRH}(T_0)] = \frac{-M_w \cdot \sum(m_{\text{solute},i} \cdot L_{\text{solute},i})(R \cdot 1000)}{(1/T - 1/T_0)},
\]

where MDRH \((T_0)\) is known (usually at \( T_0 = 298.15\text{K} \)). \( M_w \) denotes the molar mass of water, \( m_{\text{solute}} \) the molality [mole solute/kg water] of electrolyte \( i \) that deliquesces, and \( L_{\text{solute},i} \) the latent heat of fusion of salt \( i \) (RHD = MDRH, if \( i = 1 \)). \( R \) is the universal gas constant.

[15] In EQSAM we use the RHD/MDRH values of ISORROPIA according to the aerosol system considered, i.e., the ammonium-sulfate-nitrate-water system (values are given by Nenes et al. [1998]). At a relative humidity above the deliquescence point, the electrolyte is present in the aqueous phase. If the RH is above the RHD of all species considered, no solid crystalline phase of water-soluble compounds is present. Liquid/solid phase partitioning is thus determined in EQSAM according to the aerosol composition (domain) and the corresponding RHD values for binary and mixed salt solutions (Figure 1, point 2). Chemical equilibrium of individual salts is subsequently calculated for the solid (or liquid) phase, if the RH is below (or above) the temperature dependent RHD values.

2.4. Chemical Equilibrium

[16] The mass and composition of aerosols, including volatile species in the gas and aerosol phases, is calculated in EQSAM, as within all EQMs, from chemical equilibrium [Stelson and Seinfeld, 1982; Bassett and Seinfeld, 1983, 1984; Saxena et al., 1986; Pilinis and Seinfeld, 1987]. For partitioning between the gas/liquid/solid aerosol phases, chemical equilibrium is determined by the temperature dependent equilibrium constant, \( K(T) \), where \( K \) is calculated from [e.g., Denbigh, 1981]

\[
K = \Pi_i a_i^{\nu_i}.
\]
Subscript \( i \) denote an ion pair, \( a_i \) the activity, and \( v_i \) the stoichiometric coefficient. The temperature dependence and the \( K \) values used in EQSAM (Figure 1, point 3) are given by Nenes et al. [1998].

[17] To account for the effect of nonideal behavior at high ionic strength on equilibrium, \( K \) is expressed in terms of activities \( a_i \). For the gas phase, the activity is defined as \( a_i = \pi_i/p \), with \( \pi_i \) the partial pressure of compound \( i \) at atmospheric pressure \( p \).

All vapors considered (e.g., water vapor, ammonia and nitric acid) are at sufficiently low partial pressures, so that they are assumed to behave as a mixture of ideal gases. For the crystalline phase, the compound is assumed to be pure and the activity is unity, \( a_i = 1 \). In solid solutions (supersaturated solutions, where individual compounds can crystallize) the activity of the compound may be less than unity, but such cases are not considered. For the aqueous phase, the activity is defined as the product of molality \( m_i \) and activity coefficient \( \gamma_i \) of compound \( i \), i.e., \( a_i = m_i \gamma_i \).

2.5. Activity Coefficients

[18] To solve the differential equilibrium equations and gas/aerosol partitioning noniteratively, we approximate the activity coefficients of atmospheric aerosols and the ambient relative humidity in equilibrium [Metzger, 2000]. The latter work presents a more complete discussion, too. For the crystalline phase, the compound is assumed to be unity, \( a_i = 1 \). In solid solutions (domain 2), \( N = 2 \); for partly neutralized solutions containing NH\(_4\)HSO\(_4\) (domain 3), \( N = 3 \); and for nonneutralized solutions containing sulfuric acid (domain 4), \( N = 4 \).

RH denotes the fractional relative humidity \([0–1]\), and \( N \) and \( \xi \) domain specific parameters. For a theoretical interpretation of equation (3) see Appendix A.

[20] In equation (3) the domain specific parameter \( N \) (Figure 1) accounts for the number of water molecules involved in the dissolution of the salt solute of a binary or mixed solution, while \( \xi \) accounts for the charge and stoichiometric coefficient of the dissociated electrolyte. Values for \( \xi \) are given in Table 1; parameters for the parameterization of single solutes (ss) are given in Table 2. For instance, the activity coefficients of ammonium nitrate, letovicite, ammonium sulfate, or calcium sulfate can be obtained with equation (3), by using the parameters \( \xi = 4 \) for NH\(_4\)NO\(_3\), \( \xi = 2.5 \) for (NH\(_4\))\(_2\)SO\(_4\), \( \xi = 2 \) for (NH\(_4\))\(_2\)SO\(_4\), and \( \xi = 1 \) for CaSO\(_4\), with \( N \) the number of the domain: For neutralized salt solutions (domain 2) \( N = 2 \), for partly neutralized solutions containing NH\(_4\)HSO\(_4\) (domain 3) \( N = 3 \), and for nonneutralized solutions containing sulfuric acid (domain 4) \( N = 4 \). Values for \( \xi \) and \( N \) were chosen to yield an optimal fit with the results of ISORROPIA and of the EQMs presented in the following. Note that the activity coefficients of other electrolytes with similar type and charge used in various EQMs (listed in Table 2) can be obtained by using the appropriate parameters for \( \xi \) and \( N \) [Metzger, 2000]. In addition, activity coefficients can be obtained from each other, if equation (3) is used. Furthermore, equation (3) is not restricted to binary solutions. The aerosol activity and equilibrium composition of binary and mixed solutions can therefore be calculated noniteratively using equation (3).

This is possible because aerosol activity coefficients of mixed solutions do not differ significantly from those of binary solutions if the ZSR-relation is used to calculate the aerosol water content (\( a_w = RH \)). It should be noted that equation (3) is only valid for particles larger than about 0.1 micrometer since the Kelvin-term is neglected (for \( a_w = RH \)); the complete equation reads: \( a_w + 2\sigma \cdot V_{aw}/(RT \cdot r) = RH \) [e.g., Warneck, 1988]. Note further that equation (3) does not include a temperature dependency; the latter is included through equilibrium (see below).

Table 1. Parameters for Equation (3) for Major Inorganic Aerosol Compounds as Considered in Various EQMs (e.g., ISORROPIA and SCAPE)*

<table>
<thead>
<tr>
<th>( \xi )</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>NH(_4)NO(_3), NaNO(_3), KNO(_3), NH(_4)HSO(_4), NaHSO(_4), KHSO(_4), NACI, KCl, HCl</td>
</tr>
<tr>
<td>2.5</td>
<td>(NH(_4))(_2)SO(_4), (NH(_4))-H(SO(_4)), (NH(_4))-H(SO(_4))-NH(_4)H(SO(_4)) (letovicite)</td>
</tr>
<tr>
<td>2</td>
<td>(NH(_4))SO(_4), CaCl(_2), MgCl(_2), K(_2)SO(_4)</td>
</tr>
<tr>
<td>1</td>
<td>CaSO(_4), MgSO(_4)</td>
</tr>
</tbody>
</table>

*Parameter \( N \) of equation (3) is given in Figure 1 (point 1). For neutralized salt solutions (domain 2), \( N = 2 \); for partly neutralized solutions containing NH\(_4\)HSO\(_4\) (domain 3), \( N = 3 \); and for nonneutralized solutions containing sulfuric acid (domain 4), \( N = 4 \).

\( 2.5 (\text{NH}_4)_3\text{H}(\text{SO}_4)_2 = (\text{NH}_4)_2\text{SO}_4\cdot\text{NH}_4\text{HSO}_4 \) (letovicite)

Table 2. Parameters for the Parameterization of Single Solute (ss) Molalities (Figure 1)*

<table>
<thead>
<tr>
<th>Species (i)</th>
<th>( M_i )</th>
<th>( v_i^{e} )</th>
<th>( z_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH(_4)NO(_3)</td>
<td>80</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>NH(_4)HSO(_4)</td>
<td>115</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>(NH(_4))(_2)SO(_4)</td>
<td>132</td>
<td>27</td>
<td>0.75</td>
</tr>
<tr>
<td>(NH(_4))-H(SO(_4))</td>
<td>247</td>
<td>9</td>
<td>1</td>
</tr>
<tr>
<td>H(_2)SO(_4)</td>
<td>98</td>
<td>4</td>
<td>0.5</td>
</tr>
</tbody>
</table>

*The parameters are discussed in more detail by Metzger [2000].
We cannot a-priori predict if equation 3 would also hold for other aerosol systems, for which we did not have existing EQM results available. However, the $\gamma_i^{\pm}$-RH relationship (equation (3)) allows us to reproduce activity coefficients of various neutralized salt solutions including ammonium, sulfate, nitrate, sea salt and mineral dust components relative to various state-of-the-art EQMs. These EQMs calculate $\gamma_i^{\pm}$ based on the widely used activity coefficient calculation methods of Bromley [1973], Pitzer and Mayorga [1973], and Kusik and Meissner [1978]. The EQMs to which we refer in the following (section 3), i.e., MARS [Saxena et al., 1986; Binkowski, 1991] and SEQUILLIB [Pilinis and Seinfeld, 1987] use the Pitzer method for the calculation of binary activity coefficients, and the Bromley method for the calculation of multicomponent activity coefficients. SCAPE [Kim et al., 1993a, 1993b; Kim and Seinfeld, 1995] and SCAPE2 [Meng et al., 1998] have an option to use either one of the three methods, while ISORROPIA [Nenes et al., 1998] makes use of all three methods depending on the aerosol composition. A comparison of these methods is presented by Kim et al. [1993a, 1993b], Kim and Seinfeld [1995], in addition to Saxena and Peterson [1981]. Note that most of the methods that predict the activity coefficients of a multicomponent solution are empirical or semiempirical, and typically use the activity coefficients of single-electrolyte solutions of the same ionic strength. In EQSAM, we use equation (3) to obtain the activity coefficients needed in EQSAM (Figure 1, point 4). In section 3, we discuss the results of a model comparison of EQSAM with various other EQMs presently is use, including a parameterized version of the state-of-the-art EQM ISORROPIA. For the latter we substitute the original and iterative activity coefficient calculation method by equation (3), which yield a noniterative alternative for large-scale applications.

The types of activity coefficients are shown in Figure 2, plotted as a function of relative humidity. The black lines represent the $\gamma_i^{\pm}$ of SCAPE (using the Pitzer-method), the gray lines are obtained using equation (3). Generally, the activity coefficient departs for a given RH further from unity as the charge carried by the species increases. From top to bottom the types of activity coefficients represent NH$_4$NO$_3$, (NH$_4$)$_3$H(SO$_4$)$_2$, (NH$_4$)$_2$SO$_4$ and CaSO$_4$. The $\gamma_i^{\pm}$ - RH relationship (Figure 2) shows that the mean activity coefficients of salt solutes approaches one as the fractional relative humidity approaches one, owing to the increasing dilution with increasing RH, which is caused by the equilibrium growth due to water uptake.

The activity coefficients calculated with equation (3) are within the range of the activity coefficients given by various EQMs. Note that this is also true for cases where the relative humidity is not the only variable (temperature and input concentration are kept constant in Figure 2). The reason is that temperature variations and a concentration range do not significantly influence the aerosol activity coefficients for a given RH in thermodynamic equilibrium, assuming $a_w = RH$. Under this assumption, the water uptake is proportional to the total amount of dissolved matter, while the temperature affects the $\gamma_i^{\pm}$ most noticeably due to changes in aerosol composition, i.e., when evaporation or crystallization occurs (when RH equals RHD). However, evaporation or crystallization also changes the total amount of dissolved matter, which is accounted for by the use of different domains.

The appropriate activity coefficients can therefore be obtained by using a domain specific parameter N, which accounts for all salt solutes under consideration. Nevertheless, equation (3) breaks down for a sulfuric acid solution (at least compared to uncertain results of other EQMs). Fortunately, for aerosol equilibrium calculations we can neglect the activity coefficients of strongly acidic aerosols since volatile species, such as ammonium nitrate, cannot, or, are at least not assumed to be present in this case. Furthermore, the amount of water associated with the aerosol is also not affected; the amount of water solely depends on the amount...
and type of dissolve matter, which remains in this case aqueous independent of the activity (it is sufficient to treat a sulfuric acid solution as nonvolatile and noncrystalline).

2.6. Aerosol Composition

[25] Gas/aerosol partitioning only occurs for volatile and semivolatile aerosol compounds. For the ammonium-sulfate-nitrate-water aerosol system it is only relevant to the ammonium nitrate salt. However, according to the assumption made by using domains, this salt can only form if surplus ammonia is available, which is the case if sulfate is completely neutralized (domain 2 in Figure 1). All other ammonium salts and nonneutralized sulfate (sulfuric acid) are treated as nonvolatile.

[26] In addition, sulfuric acid is assumed to remain in the aqueous phase regardless of its solute activity and activity coefficients. Thus, these assumptions allow simplifications with respect to the explicit determination of the various sulfate states, i.e., \( H_2SO_4 \), \( HSO_4^- \), \( SO_4^{2-} \). To increase the computational efficiency we directly determine the sulfate states in EQUAM (denoted as \( \Gamma \) at point 1 in Figure 1), based on the ammonium to sulfate mole ratio (domain). The use of domains thus yields the number and order of the equilibrium reactions, and the stoichiometric coefficient of sulfate. The latter is needed to determine the neutralization by ammonia, and the aerosol water mass associated with ammonium sulfate, ammonium bisulfate, or sulfuric acid.

[27] If sufficient ammonia is available to neutralize all sulfate (domain 2), the residual amount of ammonia might neutralize nitric acid to form ammonium nitrate. Depending on the relative humidity and temperature, it is determined in the subdomain whether the RH exceeds the RHD of ammonium nitrate (Figure 1, point 2), or, if hysteresis is considered, the history of the aerosol compounds is taken into account as well (see M2002 for the definition and the time dependency). Then, either gas-liquid, or gas-solid equilibrium is calculated, if the partial pressure product of gaseous ammonia and nitric acid exceeds the value given by the corresponding temperature dependent equilibrium constant (Figure 1, point 3). For the aqueous phase, the activity coefficient and the single solute (ss) molalities are calculated with parameterizations, i.e., equation (3) within point 4 and point 5 of Figure 1, respectively, so that the equilibrium equations can be solved directly. From the total amount of aerosol nitrate, the residual amount of the nitric acid can be determined. The residual amount of the nitric acid and ammonia finally yield the gas phase concentrations, while the sum of ammonium, sulfate and nitrate yield the total particulate matter (Figure 1, point 6). For the aqueous phase, the amount of water associated with the aerosol is determined (Figure 1, point 7, Metzger [2000]).

[28] Note that because of the \( \gamma \) -RH relationship (equation (3)), single solute molalities and aerosol water can be parameterized; the single solute molalities are presently obtained from tabulated measurements in EQMs. The single solute molalities are expressed in terms of relative humidity (Figure 1, point 5). They are used to calculate the water mass of the aerosol upon substitution of the expression for molality in the definition of aerosol water by using the ZSR-relation (Figure 1, point 7). For illustration and further discussion of these empirical parameterizations we refer to Metzger [2000].

2.7. Model Summary

[29] Figure 1 gives an example of the structure of EQSAM and can be summarized as follows: Row 1 defines the division in domains according to the mole ratio of total ammonia (t denotes total = sum of ammonia and ammonium) and total sulfate (sum of sulfuric acid and sulfate), for which certain parameters are defined for the parameterizations; i.e., the domain number N in column 1 and the stoichiometric coefficient \( \Gamma \) of ammonium in column 4 (both row 1). The concentration of free ammonia (superscript F) is determined, i.e., the amount of ammonia which is available after the neutralization of total sulfate by using \( \Gamma \) depending on the domain. For a given domain (here domain 2, where sulfate is neutralized), gas/aerosol partitioning can occur. Depending on the subdomain (determination in row 2), i.e., whether the relative humidity (RH) is below or above the temperature dependent relative humidity of deliquescence (RHD) of a given aerosol composition (domain), partitioning between the gas and solid or liquid aerosol phase is considered; row 2–9 is therefore divided into a left and a right column, respectively. Note that the RHD is considered for single salt compounds (e.g., ammonium nitrate), while the mutual deliquescence relative humidity (MDRH) is used for mixed salts (e.g., a mixture of ammonium sulfate and ammonium bisulfate). According to the domain and subdomain the appropriate temperature dependent equilibrium constant is used to calculate either gas-solid or gas-liquid equilibrium (row 3).

For the former case, i.e., RH<RHD, the activity coefficient is 1 and, e.g., solid ammonium nitrate (subscript s) is in equilibrium with free ammonia and total nitric acid (t denotes the sum of nitrate and nitric acid). For the case RH>RHD, the activity coefficient is directly derived from equation (3) (row 4). Additionally, the solution molalities are derived from parameterizations (row 5), which depend for a given RH only on the type of (salt) solute (since the amount of water and solute are proportional). The equilibrium concentration are then determined in row 6: for the gas/aerosol partitioning of ammonium nitrate, gaseous nitric acid is determined as the residual after neutralization of total nitric acid by the concentration of ammonium (in equilibrium with nitrate); likewise, the amount of residual gaseous ammonia is determined as the difference between free ammonia and nitrate, while the determination of sulfuric acid additionally depends on \( \Gamma \). Subsequently, the solid or aqueous concentrations of ammonium and sulfate are calculated, as well as the dry or aqueous particulate matter (PM) and the total PM (t denotes sum of solid and aqueous PM; the subscript s and aq denotes solid and aqueous, respectively). The amount of aerosol water (W) and the approximate radius increase (\( r_{inc} \), caused by the water uptake, are determined in row 7 (for the wet case). The proton concentration (H+) is calculated in row 8 and the ionic strength (I) of the solution in row 9. Row 10 defines the diagnostic output for both the solid and aqueous case. All diagnostic output will be discussed in the next section.

3. Equilibrium Model Comparison

[30] In this section we compare EQSAM with other EQMs in use. We present results of a model comparison for different modeling tasks, using various equilibrium models presented in section 2.5 (i.e., MARS, SEQUILIB, SCAPE, SCAPE2, ISORROPIA). Since SCAPE has the
option to choose different activity coefficient calculation methods (ACCM), i.e., the Pitzer Method (PM), Kusik-Meissner Method (KM), or Bromley Method (BM) (introduced in section 2.5), we will use these for the model comparison to investigate the differences caused by different ACCMs. The different SCAPE models will be termed according to the ACCM used: SCAPEa-PM (SCAPE), SCAPEb-KM (SCAPE2), SCAPEb-BM (SCAPE2). Unfortunately not all versions were numerically stable under all conditions, therefore only combinations have been used which yield reliable results. The comparison includes a parameterized version of ISORROPIA, denoted by the suffix 'P'. In ISORROPIA-P we have replaced the original ACCM by the activity coefficient - RH relationship used in EQSAM, i.e., equation (3) as described in section 2.5.

[32] The comparison is performed on three levels: (1) In box model calculations, all EQMs are applied to an artificial though realistic set of input data, using fixed concentrations and temperature, so that the results (differences) can be studied as a function of RH. (2) In global offline calculations, all EQMs are applied to global chemistry fields (10°x7.5° resolution) as produced with an atmospheric/chemistry transport model (TM3) and ECMWF meteorology using monthly mean surface values for January 1997; this allows a study of the differences for a wide range of realistic atmospheric conditions, i.e., temperature, relative humidity and various aerosol precursor concentrations. (3) In global online calculations, EqsAM and ISORROPIA have been incorporated into the atmospheric/chemistry transport model TM3 to calculate the gas/aerosol partitioning online, i.e., interactively with the other chemistry simulations, accounting for feedback between the gas and aqueous phase (including cloud phase chemistry), transport and deposition processes (as described by M2002).

3.1. Box Model Calculations

[33] To explore the errors introduced by using EqsAM relative to the more comprehensive EQMs in use, we first compare the models for three cases of selected input concentrations of the ammonium/sulfate/nitrate/water-system, which corresponds to three different concentration domains, i.e., ammonium/sulfate ratios (section 2.2). The results of the gas/liquid/solid equilibrium partitioning will be shown as function of RH (10–95%). The input concentrations [μmol/m³] have been fixed to the following: tSO₄⁴⁻ / tNO₃⁻ / tNH₃ for (domain = 4 / 3 / 2), tNH₃ = 0.4, and tNO₃⁻ = 0.1. The prefix t denotes total gas and aerosol concentration; the temperature has been fixed to T = 20°C.

[34] In the light of global modeling we focus here on the gas/aerosol partitioning of nitrate and ammonium, the degree of neutralization, the total (nonwater) particulate matter, the aerosol associated water mass, and the approximated radius increase due to water uptake (Figure 1).

[35] The results of this model comparison are shown in Figure 3 as a function of RH (10–95%) for each domain. The comparison shows that nitrate and ammonium partitioning is predicted for all domains by all models and all ACCM versions with differences smaller than a few percent. While nitric acid partitions almost completely into nitrate only at relative high humidities above 90% for the case of surplus ammonia (domain 2), ammonia remains in the aerosol phase independently from RH if sulfate is not completely neutralized by ammonium (domain 3 and 4). Only for domain 2, ammonia partitioning occurs by RH dependent ammonium nitrate formation. Note that EqsAM follows the reference model ISORROPIA very well, which is presently the most sophisticated model in terms of accuracy and computational performance. MARS, on the other hand, is the simplest of all equilibrium models and shows the largest deviations from other models predictions. Remarkably, the parameterized version of ISORROPIA (ISORROPIA-P) shows also (as EqsAM) only small deviations from the original version. Note that the iterative structure of the ISORROPIA-P was kept unchanged to minimize errors associated with other aspects than the ACCM.

[36] According to Figure 3 the relatively strongest differences between all EQMs occur for the sulfate neutral case (domain 2). Nevertheless, differences are overall rather small and EqsAM follows closely ISORROPIA for all cases. Note that the uptake of aerosol water is strongest for the ‘sulfate very rich case’ (domain 4), because nonneutralized sulfuric acid exists in the aerosol phase. This causes water uptake at a relative humidity even below 10%, since sulfuric acid is always associated with water. For the other cases (domain 2 and 3) water uptake takes place only if the relative humidity exceeds the lowest deliquescence relative humidity of the corresponding salt solution, or the lower limit of the mutual deliquescence relative humidity range. Although water uptake is strong for domain 4, the radius increase due to water uptake is not. The reason is that the radius increase is proportional to the ratio of total particulate matter (including aerosol water) and the total dry particulate matter (approximately to a power of 1/3 to obtain the radius from mass).

Because the aerosol water mass is proportional to the dry particulate matter, the main differences in water uptake and radius increase are confined to the relative humidity range where solid particles can form. However, this is also the humidity range where the main differences between all models occur. The aqueous phase is determined for the gas/liquid/solid equilibrium calculations by the relative humidity of deliquescence (section 2.3), for which different assumptions are used for different EQMs. For instance, ISORROPIA uses temperature dependent mutual deliquescence ranges for salt mixtures, which are also used in EqsAM (according to the aerosol system considered). All other models use RHD values only for individual salts. RHD values for individual salts generally lead to the formation of solid particles at a higher RH. Additionally, MARS and SEQUILIB do not account for the temperature dependence of RHDs.

[37] We thus note that the difference in deliquescence humidity used in various EQMs is the main cause of deviations associated with the prediction of aerosol water. To a much lesser extent, differences in the prediction of the solute concentration (at a given RH near the RHD) are responsible for the fact that some EQMs predict solids while others do not. Similarly, any failure in predicting solids due to differences in the activity coefficient calculation or the numerical stability in reaching convergence in iterative processes is negligible compared to the failure caused by differences in the RHDs. This is demonstrated by the comparison of ISORROPIA-P with the other EQMs (Figure 3).

[38] Because the main differences in the gas/aerosol partitioning calculations are associated with the assumptions on the deliquescence relative humidity, another source of
Figure 3. Comparison of equilibrium calculations of EQSAM with various EQMs in use (ISORROPIA, SEQUILIB, MARS, SCAPEa-PM, SCAPEb-KM, SCAPEb-BM), including a parameterized EQM (ISORROPIA-P). Results are shown for domains 2–4 as a function of relative humidity (10–95%). Figure 3a shows the percentage for nitrate- (top) and ammonium- (middle) partitioning, and the degree of neutralization (bottom), and Figure 3b shows the total particulate matter (top), the aerosol-associated water (middle), and the radius increase due to water uptake (bottom).
uncertainty needs to be discussed and quantified, i.e., the hysteresis effect of aerosols. Many salt solutes exhibit hysteresis, which is that they do not crystallize at the same RH at which they deliquesce. Instead, these compounds remain in a metastable supersaturated aqueous phase, rather than forming solids once they have been wet. Especially for hygroscopic particles at midlatitudes or marine environments, where the relative humidity generally exceeds the deliquescence points of the salts of interests (at least at night), the hysteresis effect of aerosols can become impor-
tant. Therefore we have quantified in Figure 4 the differences for the aerosol water associated with metastable aerosols (gas/liquid partitioning), in addition to the aerosol water shown in Figure 3, where the aerosol water is associated with the full gas/liquid/solid partitioning. However, in Figure 4 only the results of EQSAM and ISORROPIA are included; all other EQMs do not account for metastable aerosols. The main result is that differences between both models are negligible compared to the differences in the total amount of aerosol water associated with either the gas/liquid/solid or the gas/liquid partitioning. Furthermore, also the absolute difference between both models is acceptably small for global modeling applications (with respect to other model uncertainties, e.g., those associated with the parameterization of the boundary layer; see discussion in M2002). Note that the maximum values in Figure 4 are the same as before but they have been truncated to highlight the differences that only occur at water masses below 50 $\mu$g/m$^3$ (due to the effect of deliquescence).

3.2. Global Offline Calculations

[39] In this section we extend the previous comparison to a wide range of realistic atmospheric conditions so that we can quantify the relative errors for different aerosol concentrations and temperatures.

[40] We now apply all EQMs to global fields of a CTM (TM3) and meteorological fields from ECMWF, focusing on monthly mean values for January 1997 at the surface. The global chemistry fields were calculated on a horizontal $10^\circ \times 7.5^\circ$ grid, the TM3 version used is described by Houweling et al. [1998] and Lelieveld and Dentener [2000], and in more detail by M2002.

[41] Figure 5 shows the results of the model comparison for the gas/liquid/solid equilibrium calculations. We focus on the mole ratio of aerosol nitrate and sulfate (upper panels), the aerosol radius increase owing to water uptake (middle panels), and the nitrate partitioning (lower panels). Each set is shown for a rural location ($10^\circ$E, $50^\circ$N) in Germany (left), a regional average over Europe (middle), and the global average (right); for January 1997 at surface level. The EQMs are shown along the $x$ axis, i.e., from left to right EQSAM, ISORROPIA, SEQUILIB, MARS, SCAPEa-PM, SCAPEb-KM, SCAPEb-BM, ISORROPIA-P (01Z to 08Z, respectively). The main results are that the deviations associated with aerosol predictions of EQSAM are small relative to ISORROPIA and other EQMs. The same is true for the parameterized version of ISORROPIA (02Z vs. 08Z). The effect on the gas/aerosol partitioning is rather small for all models, and in particular smaller than the differences associated with different EQMs. Accordingly, the two different iterative ACCMs applied to the SCAPEb EQM yields consistent results, indicated by the comparison of the results of SCAPEb-KM (06Z) and SCAPEb-BM (07Z). In addition, the comparison of the results for the location in Germany with the results of the regional and global average further shows that the differences between EQSAM and ISORROPIA are smallest for the global average. This suggests that the results of both models are also in good agreement (or even better) for locations outside of Europe, where in particular semivolatile ammonium nitrate is less predominant. However, the differences for the single grid box are also small; about a per mille for the nitrate/sulfate mole ratio and the nitrate partitioning, and a few percent for the radius increase. The absolute values for this location furthermore indicate that nitric acid is predicted to partition almost completely into the aerosol phase under northern hemispheric winter conditions, so that the aerosol nitrate concentrations are twice as high as the sulfate concentrations. On the regional scale, the mean nitrate concentration is comparable to the sulfate concentration, which is associated...
1 Grid box (Germany)  

Europe (average)  

Global average  

mole ratio Nitrate / Sulfate (p)  

radius increase = \((\text{H}_2\text{O}/\text{PMt+1})^{1/3}\)  

nitrate partitioning = \(\text{NO}_3^-/\text{TNO}_3\) [%]
with considerable nitrate partitioning of about 70% into the aerosols over Europe. Although these values are much less for the global average, approximately 20% for the nitrate partitioning and about 33% for the nitrate/sulfate mole ratio, they indicate that gas/aerosol partitioning is important on a global scale.

[42] To investigate these differences in greater detail, we have plotted in Figure 6 the global patterns (upper panel) as predicted by EQSAM (color scale) and ISORROPIA (contour) for the total particulate matter; the middle panel shows the corresponding differences of EQSAM-ISORROPIA, and the lower panel the scatterplot, including the grid box area-weighted (left) and nonweighted (right) correlation coefficients for January 1997 at the surface. Note that the grid box area-weighted correlation coefficient accounts for the decrease of the grid box area with increasing latitude. If both differ, this indicates that they include nonzero values at northern latitudes, e.g., that gas/aerosol partitioning takes place; the absolute difference additionally indicates the relative importance of the northern latitudes. In accord with the previous findings, differences are overall rather small, and limited to locations with rather extreme atmospheric conditions, i.e., a high temperature and low relative humidity. Under these conditions hygroscopic aerosols favor the solid phase. The prediction of crystalline particles however strongly depends on the assumptions about the deliquescence points, as mentioned before. Uncertainties associated with the deliquescence points explain most of the differences, which are basically limited to the occurrence of solids. However, for these dry cases the solute activity is usually high and likely to exceed the range for which the activity coefficient calculation methods are tested (i.e., 30M for the Pitzer method). The results of ISORROPIA and the other EQMs may also be questioned for these conditions.

[43] Since the differences are mostly associated with the calculations of solids, and because of the hysteresis effect of aerosols, it is probably appropriate to limit the gas/aerosol calculations in global modeling to metastable aerosols, rather than to include the calculation of solids without considering hysteresis, unless hysteresis is explicitly calculated (to include solids alone seems insufficient according to the discussion above). For this reason, Adams et al. [1999] also followed this approach, focusing on metastable aerosol calculations with a general circulation model (GCM). Adams et al. [1999] nevertheless devote roughly three quarters of the total processor time to the thermodynamic equilibrium calculations by ISORROPIA. This would even have been much more if they would have accounted for the full gas/liquid/solid partitioning calculations.

3.2.1. CPU Time

[44] Table 3 shows the CPU time used by all EQMs applied at two different platforms. The parameterized version of ISORROPIA is included, although the iterative structure was not adapted to the activity coefficient parameterizations and therefore not optimized with respect to the CPU time consumption (to minimize errors not related to this modification as mentioned before). Nevertheless, ISORROPIA-P also shows a gain in computing time, which is caused by the fact that fewer iterations are needed to reach convergence. However, the largest gain in computational performance is achieved with EQSAM. The computational burden is about 1–2 orders of magnitude less compared to the nonparameterized EQMs. The large gain in CPU-time results from the noniterative calculation of the gas/liquid/solid aerosol partitioning with EQSAM; this model version is not even numerically optimized for this particular application. Note that the average CPU-time by iterative models strongly depends on the atmospheric conditions, i.e., the number of cases where solids must be calculated. For the same reason the average CPU-time depends on the assumptions made on the gas/aerosol partitioning (metastable or gas/liquid/solid aerosols). Moreover, also the hardware architecture on which the computations are performed can have a strong impact on the computational burden, as shown by the results in Table 3; the left side shows the computing times for the calculations performed on a personal computer (PowerBook G3) with a 250MHz CPU running under Mac OS 9, and the right side for the same calculations performed on a supercomputer infrastructure of a CRAY-C916/121024. The columns show the computational burden, i.e., CPU seconds for 8640 grid boxes (36 × 24 horizontal grids; 10 vertical levels). From the comparison of the right and left columns of Table 3 it becomes apparent that the EQMs in use are not efficient for the present generation of supercomputers with vector architectures, such as the CRAY-C916. EQMs are purely scalar and too complex for vectorization. Global modeling however largely takes place on supercomputers because of the large amount of data needed and produced. The use of vector architectures strongly limits the application of EQMs. Although all EQMs in use were developed for incorporation in larger air-quality models, they are not numerically efficient because the gas/ aerosol partitioning is solved iteratively. This limitation will remain also for the next generation supercomputers, whether they are based on scalar or vector architectures. Because pure scalar models generally perform poorly on a vector computer, it is not very surprising that even a personal computer outperforms a supercomputer (by a factor of 4 or so for scalar models), which is true even for the most efficiently optimized EQM (ISORROPIA). The parameterized model EQSAM, on the other hand, performs better on a vector machine, i.e., by a factor of 3 or so for the version including solids, and up to 3 orders of magnitudes for the reduced version excluding solids as compared to ISORROPIA (due to vectorization).

3.2.2. CPU Burden of a 1 Year Simulation

[45] For a one year integration on a coarse grid resolution (10° × 7.5°) with 19 vertical levels and a 2 hours time step

Figure 5. (opposite) Comparison of equilibrium calculations with EQSAM and various EQMs in use, including a parameterized EQM. Each point of the x axis represents a model, i.e., from left to right EQSAM, ISORROPIA, SEQUILIB, MARS, SCAPEa-PM, SCAPEb-KM, SCAPEb-BM, ISORROPIA-P (01Z to 08Z, respectively). Shown are the mole ratio of aerosol nitrate and sulfate (upper panels), the aerosol radius increase due to water uptake (middle panels), and the nitrate partitioning [%] (lower panels); for a rural location in Germany (left), a regional average over Europe (middle), and the global average (right); for January 1997 at the surface.
Figure 6. Comparison of EQSAM with ISORROPIA for the total particulate matter. The upper panels show the global pattern (color scale EQSAM, contour ISORROPIA), the middle panels show the corresponding difference between EQSAM and ISORROPIA, and the lower panels show the scatterplot, including the regionally weighted and unweighted correlation coefficients; for January 1997 at the surface.
for the chemistry/equilibrium calculations (gas/liquid/solid partitioning), which already yields a total number of calls to the equilibrium routine of the order of many millions (71.90208E+06), the computational burden for EQSAM on the CRAY would be about 43 min. Correspondingly, 139 hours would be needed for ISORROPIA, and of about 6 hours for the parameterized version (ISORROPIA-P). Note that these numbers refer to the lower limit. The actual integration by an iterative model usually consumes more computing time due to the dependence of the solid calculations on the atmospheric condition as mentioned before (these numbers were based on monthly mean values for January 1997). However, the same calculations with the EQM SCAPEb would add up to 400 hours CPU-time, therefore, ISORROPIA is already regarded as computationally efficient (and accurate). Nevertheless, our comparison shows that for global applications alternatives are desired and feasible (e.g., EQSAM), despite increasing computing power. Especially for climate calculations, where hundreds of years of simulations must be performed, parameterizations are needed. Even if the gas/aerosol calculations are limited to metastable aerosols the computational burden for ISORROPIA remains too high, i.e., of about 22.5 hours per year. This is a factor 10 more compared to the entire computing time consumption of the atmospheric/chemistry transport model TM3 (introduced in section 3.2 and described in more detail in M2002). Contrary to Adams et al. [1999], who have coupled ISORROPIA to a GCM by using prescribed HNO3-fields from a CTM, we calculate the gas/aerosol equilibrium of the ammonium/sulfate/nitrate/water-system online with the gas-phase and cloud chemistry. This therefore includes feedback of nitrate and ammonium partitioning with the gas-phase chemistry. The online calculations are performed on a 10° × 7.5° horizontal resolution, with 19 vertical levels and a 2 hour time step for gas- and aerosol phase chemistry. Following Adams et al. [1999] we only consider metastable aerosols.

Table 3. CPU Times

<table>
<thead>
<tr>
<th></th>
<th>CPU Seconds (Burden*)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Mac Pb-G3 (250 MHz)</td>
<td>Cray-C916</td>
</tr>
<tr>
<td>EQSAM</td>
<td>0.94</td>
<td>0.31</td>
</tr>
<tr>
<td>ISORROPIA</td>
<td>14</td>
<td>60</td>
</tr>
<tr>
<td>SCAPEb</td>
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<td>64</td>
</tr>
<tr>
<td>MARS</td>
<td>8</td>
<td>12</td>
</tr>
<tr>
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<td>49</td>
</tr>
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<td>SCAPEb-KM</td>
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<tr>
<td>SCAPEb-BM</td>
<td>38</td>
<td>172</td>
</tr>
<tr>
<td>ISORROPIA-P</td>
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<td>Gas/Liquid/Solid Aerosol Partitioning</td>
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<td>9.7</td>
</tr>
<tr>
<td>ISORROPIA</td>
<td>1.7</td>
<td>3.3</td>
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</table>

Metastable Aerosols

|                        |                        |                 |
| EQSAM                  | 0.93                  | 0.28            |
| EQSAMb                 | 0.88                  | 0.0048          |
| ISORROPIA             | 3.1                   | 9.7             |
| ISORROPIA-P            | 1.7                   | 3.3             |

*Number of gridboxes = 8640 (values are rounded).
*Double precision was omitted on the CRAY for ISORROPIA (ISORROPIA-P) to achieve better performance.

3.3. Global Online Calculations

In the previous subsections we have shown that the results of the aerosol calculations based on EQSAM are well within the range of the results of various EQMs in use. To extend the comparison to global modeling and to test the stability of the previous results by integration over time and various altitudes, we further compare the results of EQSAM and ISORROPIA in so-called online calculations. Thus both equilibrium models were incorporated into the atmospheric/chemistry online model TM3, for example, uses about 650 CPU seconds per month or ~2 hours per year, without thermodynamic gas/aerosol calculations. The reduced version of EQSAM, without the option for solid calculation, only adds 3.5 CPU seconds per month.

3.4. Global Online Calculations

In the previous subsections we have shown that the results of the aerosol calculations based on EQSAM are well within the range of the results of various EQMs in use. To extend the comparison to global modeling and to test the stability of the previous results by integration over time and various altitudes, we further compare the results of EQSAM and ISORROPIA in so-called online calculations. Thus both equilibrium models were incorporated into the atmospheric/chemistry transport model TM3 (introduced in section 3.2 and described in more detail in M2002). Contrary to Adams et al. [1999], who have coupled ISORROPIA to a GCM by using prescribed HNO3-fields from a CTM, we calculate the gas/aerosol equilibrium of the ammonium/sulfate/nitrate/water-system online with the gas-phase and cloud chemistry. This therefore includes feedback of nitrate and ammonium partitioning with the gas-phase chemistry. The online calculations are performed on a 10° × 7.5° horizontal resolution, with 19 vertical levels and a 2 hour time step for gas- and aerosol phase chemistry. Following Adams et al. [1999] we only consider metastable aerosols.

Since the largest uncertainties, which are associated with thermodynamic gas/aerosol calculations, arise at higher temperatures, we focus on a comparison of EQSAM and ISORROPIA for July 1997. Figure 7 shows the daily mean total direct aerosol radiative forcing at the top of the atmosphere, which is shown in Figure 7, lower panel) for the total dry aerosol mass, the aerosol associated water mass (burdens); aerosol sulfate [μgS], nitrate [μgN], and ammonium [μgN] (burdens); the residual gases nitric acid [μgN] and ammonia [μgN] (burdens); the column aerosol radiative forcing of sulfate and nitrate; and including the regionally weighted correlation coefficients. Figure 8 additionally shows scatterplots (similar to Figure 7, lower panel) for the total dry aerosol mass, the aerosol associated water mass (burdens); aerosol sulfate [μgS], nitrate [μgN], and ammonium [μgN] (burdens); the residual gases nitric acid [μgN] and ammonia [μgN] (burdens); the column aerosol radiative forcing of sulfate and nitrate; including the regionally weighted correlation coefficients. Figure 9 shows the time evolution of the aerosol radiative forcing of transported nitrate for a rural location in Germany (top), a regional average over Europe (middle), and the global average (bottom). In addition to the results of EQSAM, the differences between these results and those obtained by ISORROPIA (accordingly coupled to TM3) are included in each panel (EQSAM - ISORROPIA).

In general, relative errors introduced by the use of the computationally efficient gas/aerosol model EQSAM are also small for the online equilibrium calculations, compared to the reference model ISORROPIA. This is particularly true for the monthly mean total direct aerosol radiative forcing, which is shown in Figure 7. While the contour lines (values of ISORROPIA) nicely enclose the color-coded areas (values of EQSAM), the absolute differences are also small; differences are generally less than...
Figure 7. Online equilibrium calculations (metastable aerosols). Comparison of EQSAM with ISORROPIA, showing the monthly mean total direct aerosol radiative forcing for July 1997. The upper panel shows the global pattern (color scale EQSAM, contour ISORROPIA), the middle panel shows the corresponding difference between EQSAM and ISORROPIA, and the lower panel shows the scatterplot, including the regionally weighted and unweighted correlation coefficients.
10%, with a low scatter and a high correlation coefficient (nearly one). Furthermore, Figure 8 demonstrates that differences are also small for other aerosol properties. The relatively largest uncertainty is associated with the calculation of aerosol nitrate (Figure 8), as a result of the gas/aerosol partitioning. In contrast, differences are smallest for aerosol sulfate, because sulfate is treated as nonvolatile with the consequence that total sulfate [$\mu$gS] remains unchanged by the gas/aerosol calculations. Only the absolute sulfate mass can be affected by the equilibrium calculations (due to differences in the neutralization by ammonium), which can subsequently result in erroneous gaseous ammonia prediction and therefore of aerosol nitrate as well as the total aerosol mass and the aerosol associated water mass (which depend on the absolute mass). Nevertheless, the agreement is rather good also for these latter aerosol properties.

Note that the deviations are largest in July. In winter the overall temperature is lower and the relative humidity higher, which favors the formation of ammonium nitrate. Ammonium nitrate is then more stable, with HNO$_3$ often completely neutralized: all nitric acid simply remains in the aerosol phase in form of nitrate, without gas/aerosol partitioning (also see the discussion of Figure 2b in M2002).

To focus on the largest uncertainties, which are associated with the calculation of aerosol nitrate, we show in Figure 9 the time variability of the direct radiative forcing of nitrate, based on EqsAM, and the differences relative to ISORROPIA. The differences are largest for the rural...
July 1997 (monthly mean)

Aerosol Sulfate (Burden) $\rho_{\text{mean}} = 1$

Gaseous Nitric Acid (Burden) $\rho_{\text{mean}} = 0.99986$

Gaseous Ammonia (Burden) $\rho_{\text{mean}} = 0.999767$

Radiative Forcing of Aerosol Sulfate $\rho_{\text{mean}} = 0.999551$

Radiative Forcing of Aerosol Nitrate $\rho_{\text{mean}} = 0.98879$

Figure 8. (continued)
Figure 9. Online equilibrium calculations (metastable aerosols). Time series for July 1997 of the column aerosol radiative forcing of nitrate for a rural location in Germany (top), a regional average over Europe (middle), and the global average (bottom). The results are obtained by EQSAM (black lines). In addition, the differences between these results and those obtained by using ISORROPIA are included in each panel and marked in light gray (EQSAM - ISORROPIA). Note that the differences are very small and therefore difficult to distinguish from the minimum values.
location in Germany, although they are overall quite small. Note that the differences are negligible and therefore difficult to distinguish from the minimum values that occur at night, therefore being small as well.

[52] As mentioned above, the main source of uncertainties can be attributed to differences in the nitrate partitioning, which in turn is strongest in summer for this particular location. In general, the relative difference between EQSAM and ISORROPIA decreases as the area increases over which the averaging is performed, reflecting the nonuniform spatial distribution of the aerosol load. The strongest forcing of these anthropogenic species occurs mainly over land, i.e., over Europe, northeast America and Asia (Figure 7). A more detailed discussion of the space-time variability is presented in M2002.

[53] The online comparison thus demonstrates that the relative errors associated with the computationally efficient gas/aerosol equilibrium calculations are practically negligible for online calculations. Particularly in the light of other model uncertainties the results of the online model comparison of our computationally efficient gas/aerosol model EQSAM, as compared to the EQM ISORROPIA, are satisfactory for global modeling applications (see also the discussion in M2002).

4. Discussion and Conclusions

[54] We have introduced a simplified approach to calculate the gas/aerosol partitioning on a global scale. Our approach is based on the activity coefficient - RH relationship, which enables the solution of the nonlinear algebraic equilibrium equations noniteratively. Based on our approach we present a computationally efficient gas/aerosol model, EQSAM (Equilibrium Simplified Aerosol Model). The EQSAM thermodynamic framework is similar to the current state-of-the-art gas/aerosol models, but uses parameterizations for the calculation of the aerosol activity, including activity coefficients and water. These nonideal solution properties are usually derived iteratively in present EQMs by using time consuming numerical schemes. We have shown that the activity coefficient - RH relationship can be used to approximate the equilibrium calculations. Several studies have previously addressed the importance of aerosol hygroscopic growth [e.g., Low, 1969a, 1969b; Winkler, 1973, 1988; Hanel, 1976; Tang, 1980; Tang and Munkelwitz, 1994], but none of these were aimed at the development of a gas/aerosol model for global modeling. Nevertheless, there are studies that have explored the issue of the ammonium-sulfate-nitrate aerosol climate forcing on a global scale, for instance, those of Van Dorland et al. [1997] and Adams et al. [1999, 2001]. The former work, however, did not include an explicit determination of the aerosol composition, while in the latter an EQM was coupled to a climate model by using offline calculated chemistry fields of a CTM. We extend these studies by providing a method that can easily be used for the interactive (online) determination of the aerosol composition within global chemistry-transport and climate models. Although our method is based on equilibrium, for global modeling this assumption is reasonable. The equilibration times of relevant aerosol particles are of the order of minutes and thus much shorter than the typical time steps of 0.5–2 hours applied in CTM or GCMs to calculate chemistry and transport.

[55] To demonstrate that our simplified approach used for EQSAM yields consistent results with other EQMs, we have presented an equilibrium model comparison, including a state-of-the-art EQM (ISORROPIA) and a parameterized version of ISORROPIA. For the latter we have applied the parameterization used in EQSAM for the activity coefficient calculation, by replacing the original iterative activity coefficient calculation method by our noniterative one, i.e., equation (3). The model comparison shows that the most important aerosol properties for global modeling, such as the total particulate matter and the aerosol associated water mass, can be sufficiently accurately reproduced with respect to other model uncertainties. The results of the box-model comparison further showed that the relative errors (e.g., the differences between EQSAM and ISORROPIA) are small compared to the assumptions on the aerosol state. Especially for aerosols, the EQM ISORROPIA, while many EQMs only consider the deliquescence humidity of single salt compounds.

[56] We emphasize that the application of any EQM in global atmospheric studies is associated with considerable uncertainties. One should keep in mind that these models (including EQSAM) are based on simplifying assumptions, including thermodynamical equilibrium, which implies that the water activity of the aerosol equals the ambient relative humidity. The so-called ZSR relation is a consequence, simply assuming that the total aerosol associated water is the sum of the water fractions of all single-solute solutions. Furthermore, multicomponent aerosols are assumed to be internally mixed. To introduce and demonstrate the activity coefficient - RH relation, we only addressed submicron particles (bulk approach). The above assumptions are valid for inorganic salt compounds if the aerosol modeling is limited to the ammonium-sulfate-nitrate-water system. These assumptions are, however, no longer valid if particles such as sea-salt or mineral dust are considered. Especially the latter particles often provide a pre-existing solid core that favors condensation; heterogeneous nucleation is generally thermodynamically favored. They therefore can diurnally redistribute (semi-) volatile compounds such as ammonium nitrate from smaller particles to larger ones (those including a solid core) as the relative humidity decreases [Wexler and Seinfeld, 1990; Wexler and Potukuchi, 1998]. The equilibrium approach might fail for coarse mode particles, such as sea salt and mineral dust. The equilibration times are considerably longer for larger particles (because of the smaller surface-to-volume ratio), possibly exceeding the timescales over which transport and chemistry are calculated. Especially in remote and less polluted regions, or regions exposed to cold conditions, the equilibrium assumption may not be satisfied. In these
locations, nucleation might become important as well, which is not considered in EQMs. However, such aerosol dynamical processes can be included separately in the overall aerosol module of which the EQM is one component.

[57] Finally, the limitations of our approach should be evaluated in the light of assumptions in atmospheric chemistry and climate models (CTM or GCM). The efforts to achieve high accuracy for the gas/aerosol calculations should balance with the efforts to describe other processes in the CTM or GCM. In fact, other process descriptions may dominate the uncertainties, or affect the assumptions on which the state-of-the-art model is based so that they may not hold under all circumstances.

[58] For instance, we show in M2002 that the uncertainties associated with the activity coefficient parameterization.

**Appendix A: Theoretical Interpretation of Equation (3)**

[59] For the interested reader we present here a theoretical interpretation of our empirically derived equation (3). Although we are able to theoretically derive in the following the relationship between activity coefficients and the relative humidity, we are not able to clearly determine the uncertainties associated with the activity coefficient parameterization.

Equation (A4) yields the equilibrium constant K (section 2.4) of a given equilibrium reaction at a given temperature. Neglecting the temperature dependency, i.e., upon rearranging and exponentiation and expressing the sum of the logarithm as their product K = \( \Pi \alpha^0 \).

[60] For atmospheric aerosols in thermodynamic equilibrium with the ambient relative humidity (RH), the following reactions are of interest, which subsequently lead to the relationship between activity coefficients and RH (as used in EQSAM).

\[
\begin{align*}
\text{(R1)} & \quad \nu_{g1} \cdot (\text{NH}_4)_g + \nu_{g2} \cdot (\text{HNO}_3)_g \leftrightarrow \nu_s \cdot (\text{NH}_4\text{H}_2\text{NO}_3)_s \\
\text{(R2)} & \quad \nu_s \cdot (\text{NH}_4\text{H}_2\text{NO}_3)_s + \nu_w^+ \cdot (\text{H}_2\text{O})_q \leftrightarrow \nu_s^+ \cdot (\text{NH}_4^+)_{aq} + \nu_w^+ \cdot (\text{H}_2\text{O})_{aq} \\
\text{(R3)} & \quad 1 \cdot (\text{NH}_4\text{H}_2\text{NO}_3)_{aq} + \nu_w^+ \cdot (\text{H}_2\text{O})_q \leftrightarrow \nu_s^+ \cdot (\text{NH}_4^+)_{aq} + \nu_w^+ \cdot (\text{H}_2\text{O})_{aq}
\end{align*}
\]

R1 is determined by \( K_{\text{NH}_4\text{H}_2\text{NO}_3} \), the amount of aerosol water depends for R2 on the number of salt molecules and RH (with RH > RH\(_{\text{NH}_4\text{H}_2\text{NO}_3} \)), and for R3, additionally on the number of moles into which each mole of the electrolyte dissociates. R3 actually depends on the dissociation constant, for ammonium nitrate [see, e.g., Mozurkevich, 1993]. The stoichiometric coefficients are \( \nu_{g1} = \nu_{g2} = \nu_s = \nu_s^+ = 1, \nu_w^+ = \nu_w + \nu_w^+ = 2 \), while \( \nu_w^+ \) and \( \nu_w^+ \) are unknown.

[61] For a binary solution of an undissociated electrolyte (R2), equation (A4) yields

\[
\begin{align*}
\nu_s \cdot g_{s}^{0} + \nu_w^+ \cdot g_{w}^{0} + R \cdot T \cdot \nu_s \cdot \ln a_{s}^{0} + R \cdot T \cdot \nu_w^+ \cdot \ln a_{w}^{0} &= 0, \quad (A5)
\end{align*}
\]

where \( g_{s}^{0} \) and \( g_{w}^{0} \) represent the Gibbs free energies at the standard state temperature \( T^0 \) (and pressure \( p^0 \)) of 1 mole of solute and of 1 mole of water, respectively. The activities \( a_{s} \) and \( a_{w} \) denote the electrolyte and water, and \( \nu_s \) and \( \nu_w^+ \) their stoichiometric coefficients, respectively.

[62] Equation (A5) can be rewritten to yield (upon exponentiation)

\[
\begin{align*}
a_{s}^{\nu_s} &= a_{w}^{\nu_w^+} \cdot \exp[\nu_s \cdot g_{s}^{0} + \nu_w^+ \cdot g_{w}^{0}]/(R \cdot T). \quad (A6)
\end{align*}
\]

[63] For the formation of a pure compound (then without the terms denoted by the index w) the exponent of equation (A6) would yield the equilibrium constant \( K \), e.g., of pure ammonium nitrate (R1). However, if the reaction takes place in the aqueous phase, additionally a certain number of moles of water will condense (R2). This requires a relation to exist between the differential changes of the moles of solute and water, i.e., between \( \nu_s \) and \( \nu_w^+ \). Furthermore, in this case the exponent of equation (A6) disappears, i.e., is unity.
The required condition that the exponent of equation (A6) disappears is
\[ \nu_i = v_i \cdot g_i^0 = 0, \]  
(A7a)
so that the relation between the stoichiometric coefficients, according to (R2), is
\[ -\nu_i = v_i \cdot g_i^0 / g_w^0 = v_i \cdot N_w, \]  
(A7b)
or, if the electrolyte is dissociated (R3), i.e.,
\[ -\nu_i = v_i^+ \cdot g_i^+ / g_w^0 = v_i^+ \cdot N_w, \]  
(A7c)
with \( N_w = v_i \cdot N_w^0 \cdot k_w. \)

The relation between the stoichiometric coefficients (equation (A7b)) reduces equation (A6) with \( a_s = \gamma_s \cdot m_s \) to
\[ \gamma_s \cdot m_s = a_w^{N_s^0}. \]  
(A8a)
Similarly, for dissociation (a \( \rightarrow a^l_v = a_w^{N_s^0} = a_w^{N_s^0} \)), according to (R3) and equation (7c), i.e.,
\[ (\gamma_s^{x^+} \cdot m_s^{x^+})^{v^+} = a_w^{x^+ N_s^0}. \]  
(A8b)

The definition of molality is \( m_s = 55.51 \cdot n_s / n_w = 55.51 \cdot x_s / x_w, \) and for binary solutions \( x_s + x_w = 1. \) Here \( n_s \) and \( n_w^0 \) are the number of moles of the solute (undissociated) and water, respectively; \( x_s^0 = n_s / (n_s + n_w^0). \) Taking dissociation into account \( n_s \) becomes \( n_s^d = n_s \cdot v_i \) and \( n_w^0 \) becomes \( n_w^0 \cdot v_i, \) so that \( m_s = 55.51 \cdot n_s / n_w^0 \) becomes \( m_s^{x^+} = (55.51 \cdot n_s^d / n_w^0 \cdot x_s^0)^{v^+}. \) The sum of the mole fraction is unity and the mole fraction of the solute can be expressed by the mole fraction of the aerosol water, i.e., \( x_s^0 / x_w = (1 - x_w) / x_w = (f_w^0 / a_w^0) = (f_w^0 / a_w^0) = (f_w^0 / a_w^0 - 1), \) so that \( m_s^{x^+} = [N_w^{x^+} / 55.51 \cdot (f_w^0 / a_w^0 - 1)]^{v^+}. \) Note that we have used the definition of the activities for the solute and water on the mole fraction scale, i.e., \( a_s^{x^+} = x_s^+ \cdot f_s^+ \) and \( a_w = x_w \cdot f_w^0, \) where \( f_s^+ \) and \( f_w^0 \) denote the rational activity coefficients of the dissociated solute and water, respectively. Substitution of the mean molality \( m_s^{x^+} \) of the dissociated ion-pair into equation (A8b) gives
\[ \gamma_s^{x^+} = a_w^{x^+ N_s^0} / [N_w^{x^+} \cdot 55.51 \cdot (f_w^0 / a_w^0 - 1)]^{v^+}. \]  
(A9a)

\( \gamma_s^{x^+} \) denotes the mean activity coefficient of the dissociated salt solute. Since activity coefficients are defined to correct for ion-ion interactions, they depend on the charge density of the solution. The charge density depends in turn, for a given solute, on the total charge of the ions \( Z_s^0 \) and the amount of water molecules \( [v^0_w], \) which are associated with the formation and dissociation of the electrolyte. We therefore express the mean charge density \( \rho_s^0 = Z_s^0 / [v^0_w] \) with \( [v^0_w] \) the absolute value of \( v_w. \) The mean ion charge \( Z_s^0 \) denotes the charge of each ion, i.e., \( Z_s^0 = (2r_s^0 Z_s + \Sigma \gamma_s Z_s^0). \) Thus, considering dissociation the activity coefficient of the undissociated salt solute \( \gamma_s \) becomes \( \gamma_s^{x^+} \cdot \gamma_s^{x^-} / \gamma_s^{x_0} = \gamma_s^{x^+} / \gamma_s^{x_0} \) so that equation (9a) yields
\[ \gamma_s^+ = a_w^{N_s^0} / [N_w^0 \cdot 55.51 \cdot (f_w^0 / a_w^0 - 1)]^{v^+}. \]  
(A9b)

With (A7c) \( \rho_s^0 = Z_s^0 / [v^0_w] = Z_s^0 / (v_s^+ + v_w), \) and the water activity \( a_w \) expressed in terms of the fractional relative humidity (RH), we can finally write the mean activity coefficient \( \gamma_s^+ \) as a function of RH, i.e.,
\[ \gamma_s^+ = \rho_s^0 / [N_w^0 \cdot 55.51 \cdot (1 - \rho_s^0)]^{v^+}, \]  
(A10)

with \( \rho_s^0 = Z_s^0 / [v^0_w] = Z_s^0 / (v_s^+ + v_w), \) \( N_w^0 = v_s^+ N_w^0 k_s, N_w^0 = k_s, \) and \( z_+ = e^+ - e^- \) and \( z_- = e^- - e^+ \) where \( e^+ \) and \( e^- \) denote the positive and negative ion charge, respectively. With the above definition of \( \rho_s^0 = Z_s^0 / [v^0_w] \) and the ionic charge \( z_s^0, \) we get for major inorganic aerosol compounds, given in Table 1 for various EQMs (e.g., ISORROPIA, SCAPE), the following values for \( \rho_s^0 = 1 \) (1-1.1 + 1.1)/2 for \( NH_4NO_3, \) \( \rho_s^0 = 1.6 = (4\cdot1.1 + 1.2)/5 \) for \( (NH_4)_2SO_4, \) \( \rho_s^0 = 2(1 + 1.2)/3 \) for \( NH_4SO_4, \) and \( \rho_s^0 = 4(1 + 1.2)/2 \) for \( CaSO_4. \)

If we assume the following values for \( k_s, f_w^0, v_i, \) and \( k_w, \) according to an \( \pm \)-ion-pair; \( f_w^0 = 1, \) because \( \gamma_s^+ \) varies (both parameters account for the same solution-non-ideal behavior); \( v_i = 1, \) because of stoichiometry (condensation/evaporation of water vapor applies to each mole of the salt solute), we obtain for \( N_w^0 \) a value of 5.4. If we further make the interpretation that the parameter \( \xi \) in equation (3) is \( \xi = N_w^0 / N_w^0, \) then equation (A10) yields consistent results with equation (3) in the light of the overall general functional dependency of \( \gamma_s^+ \) on RH.

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