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ISORROPIA II: a computationally efficient thermodynamic equilibrium model for K$^+$-Ca$^{2+}$-Mg$^{2+}$-NH$_4^+$-Na$^+$-SO$_4^{2-}$-NO$_3^-$-Cl$^-$-H$_2$O aerosols

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Abstract

This study presents ISORROPIA II, a thermodynamic equilibrium model for the $K^{+}$ – $Ca^{2+}$ – $Mg^{2+}$ – $NH_4^+$ – $Na^+$ – $SO_4^{2-}$ – $NO_3^-$ – $Cl^-$ – $H_2O$ aerosol system. A comprehensive evaluation of its performance is conducted against the thermodynamic module SCAPE2 over a wide range of atmospherically relevant conditions. The two models overall agree well, to within 13% for aerosol water content and total PM mass, 16% for aerosol nitrate and 6% for aerosol chloride and ammonium. Largest discrepancies were found under conditions of low RH, primarily from differences in the treatment of water uptake and solid state composition. In terms of computational speed, ISORROPIA II was always found to be more than an order of magnitude faster than SCAPE2, with robust and rapid convergence under all conditions. The addition of crustal species does not slow down the thermodynamic calculations (compared to the older ISORROPIA code) because of optimizations in the activity coefficient calculation algorithm. Based on its computational rigor and performance, ISORROPIA II appears to be a highly attractive alternative for use in large scale air quality and atmospheric transport models.

1 Introduction

Aerosols, or airborne particulate matter (PM), play a central role in atmospheric processes. They reflect a significant amount of radiation back to space, thus enhancing the planetary albedo. Atmospheric aerosols can cause visibility impairment in highly polluted areas (Altshüller, 1984) through their interactions with electromagnetic radiation. By acting as cloud condensation nuclei (CCN), they affect cloud droplet number concentration, cloud droplet effective radius, and cloud reflectivity. Changes in aerosol concentrations also affect droplet size distribution affecting precipitation frequency and cloud lifetime. Aerosols can also be responsible for acid rain production, which can adversely affect soil and water quality, especially in environments rich in $SO_2$ and $NO_x$. It has been established that inhaled aerosol particles are detrimental to human health;
as particles can contain toxic inorganic and organic substances that are often correlated with asthma and chronic obstructive pulmonary disease (Zanobetti et al., 2000; Ramachandran and Vincent, 1999; Brauer and Brook, 1997; Schwartz, 1994). Recent studies (Kaiser, 2005) have suggested that fine particles (PM$_{2.5}$) are more effective in causing respiratory illness and premature death than larger particles due to their ability to penetrate deeper into the lung. Dockery et al. (1993), who conducted a survey on six cities over 16 years, found that people living in areas with higher aerosol concentrations had a lifespan two years less than those living in cleaner areas. The knowledge of the chemical composition and physical state of atmospheric particles may be a critical link between toxicity and particulate matter.

Atmospheric aerosols are composed of water, inorganic salts, crustal material, organics and trace metals. A large part of the particle (dry) mass is inorganic (25–50%) with ammonium ($\text{NH}_4^+$), sodium ($\text{Na}^+$), sulfate ($\text{SO}_4^{2-}$), bisulfate ($\text{HSO}_4^-$), nitrate ($\text{NO}_3^-$) and chloride ($\text{Cl}^-$) being the most important contributors to the dry inorganic PM$_{2.5}$ (Heitzenberg, 1989). Crustal species, such as $\text{Ca}^{2+}$, $\text{K}^+$, $\text{Mg}^{2+}$ are a major component of dust, hence an important constituent of ambient particles. These inorganic species may be in the form of aqueous ions, or in the form of precipitated solids, in thermodynamic equilibrium with atmospheric gases and humidity.

To compute the composition and phase state of aerosols, every atmospheric gas/aerosol model requires knowledge of the thermodynamic equilibrium state because the driving force for mass transfer of species between gas and aerosol phases is the departure from equilibrium. Performing thermodynamic equilibrium calculations for aerosol systems is a demanding computational task (e.g., Nenes et al., 1999) because it involves the global optimization of a nonlinear convex problem, or, the solution of numerous nonlinear equations. The non-linearity is stronger under conditions of low relative humidity, where aqueous aerosol solutions are strongly non-ideal and require the use of activity coefficients (which increases computational cost). Therefore, efficient and accurate solution algorithms are highly needed.

Numerous aerosol inorganic equilibrium models have been developed over the
years, differing in the chemical species that they can treat, the solution method used and the type of input they can accept. Recent examples include AIM2 (Clegg and Pitzer, 1992; Clegg et al., 1992, 1994, 1995, 1998a, b; Wexler and Clegg, 2002), SCAPE2 (Kim et al., 1993a,b; Kim and Seinfeld, 1995; Meng et al., 1995), EQUISOLV II (Jacobson et al., 1996; Jacobson, 1999a,b), ISORROPIA (Nenes et al., 1998; Nenes et al., 1999), GFEMN (Ansari and Pandis, 1999a,b), EQSAM2 (Metzger et al., 2002a, b; Metzger et al., 2006), HETV (Makar et al., 2003), MESA (Zaveri et al., 2005a, b) and UHAERO (Amundson et al., 2006). AIM2 and GFEMN use the iterative Gibbs free energy minimization method to solve equilibrium problems for $\text{NH}_4^+/\text{Na}^+/\text{NO}_3^-/\text{SO}_4^{2-}/\text{Cl}^-$ systems. UHAERO uses the Gibbs free energy minimization method (using a primal-dual method, coupled to a Newton iteration method) and offers a choice of the Pitzer, Simonson, Clegg (PSC) mole fraction-based model (Pitzer and Simonson, 1986; Clegg and Pitzer, 1992; Clegg et al., 1992) or the ExUNIQUAC model (Thomsen and Rasmussen, 1999) for the activity coefficient calculations. These models have treat either the ammonium – nitrate – sulfate system or the ammonium – sodium – nitrate – chloride – sulfate system. Even though direct minimization usually gives the most accurate results, it comes at a large computational cost (Ansari and Pandis, 1999b). MESA simultaneously iterates for all solid-liquid equilibria using a pseudo-transient continuation method and solves for the $\text{NH}_4^+/\text{Na}^+/\text{NO}_3^-/\text{SO}_4^{2-}/\text{Cl}^-$ system of species with the addition of calcium cations. EQUISOLV II sequentially solves for the root of each equation in the system of equilibrium reactions and then iterates over the entire domain until convergence. This method is ideal for the incorporation of new reactions and species with minimal programming effort, but optimal computational performance is obtained only on vectorized computational platforms (Zhang et al., 2000). EQSAM2 uses a simplified parameterization of the nonideal solution properties based on the relationship between activity coefficients and the relative humidity (Metzger et al., 1999) to solve the $\text{NH}_4^+/\text{Na}^+/\text{NO}_3^-/\text{SO}_4^{2-}/\text{Cl}^-/\text{Ca}^{2+}/\text{Mg}^{2+}/\text{K}^+/\text{RCOO}^-$ system. SCAPE2 divides the problem into several subdomains based on major species that impact equilibrium partitioning and water uptake. By always attempting to solve for a liquid phase, SCAPE2
predicts the presence of water even at very low ambient relative humidities (<10%), and for this reason often does not predict the presence of a crystalline phase (solid precipitate).

Similar to SCAPE2, ISORROPIA determines the subsystem set of equilibrium equations and solves for the equilibrium state using the chemical potential method. The code solves analytically as many equations as possible through successive substitutions; remaining equilibrium reactions are solved numerically with bisection for stability. ISORROPIA also offers the choice of using precalculated tables of binary activity coefficients and water activities of pure salt solutions, which speeds up calculations. Another important feature of the model is the use of mutual deliquescence of multi-component salt particle solutions, which lowers the deliquescence point of the aerosol phase. All the previously described models solve the “forward” problem, in which total (gas + aerosol) concentrations of chemical species along with ambient temperature and relative humidity are used as input. Besides the forward problem, ISORROPIA also offers the ability to solve for the “reverse problem”, in which known quantities are the concentrations of sodium, ammonium, nitrate and sulfate in the aerosol phase together with the ambient temperature and relative humidity. Being computationally efficient, ISORROPIA has proved to be the model of choice for many three-dimensional air quality models (CMAQ, CAMx, etc.), chemical transport and general circulation models (Ansari and Pandis, 1999b; Yu et al., 2005). HETV is based on the algorithms of ISORROPIA for sulfate, nitrate and ammonium aerosol systems and is optimized for running on vectorized computational architectures.

An important drawback of the above codes (with the exception of SCAPE2, EQUISOLV II and EQSAM2) is lack of treatment of crustal species (Ca, K, Mg). It has been shown (Jacobson, 1999b; Moya et al., 2001b) that the inclusion of crustal species in a thermodynamic equilibrium framework can be important in modeling size/compositional distribution of inorganic aerosols. An attempt to treat crustals as “equivalent sodium” was met with modest success (Moya et al., 2001a) provided that Ca was a relatively small fraction of aerosol dry mass.
In the current study, we present a new model, “ISORROPIA II”, in which the thermodynamics of the crustal elements of calcium, potassium and magnesium have been added to the preexisting suite of components of the computationally efficient ISORROPIA. The new model, combining the computational advances with the explicit thermodynamics of crustals, is compared against the predictions of SCAPE2, both in terms of speciation and computational requirements.

2 Thermodynamic equilibrium calculations

2.1 Equilibrium constants

In a closed (aerosol-gas phase) system composed of $i$ chemical species and $j$ reactions at constant temperature $T$, and pressure $P$, the Gibbs free energy of the system, $G$, is minimum at chemical equilibrium. This condition is equivalent to stating that the system of reactants is equal to that of products, which can be written as (Nenes et al., 1998):

$$\prod_{i} a_{i}^{v_{ij}} = K_{j}(T)$$

(1)

where $a_{i}$ is the activity of species $i$, $v_{ij}$ is the stoichiometric coefficient of species $i$ participating in the reaction $j$, and $K_{j}$ is the equilibrium constant of the $j$-th reaction at temperature $T$,

$$K_{j}(T) = \exp \left[ -\frac{\sum_{i} v_{ij}\mu_{i}^{o}(T)}{RT} \right]$$

(2)

where $R$ is the universal gas constant and $\mu_{i}^{o}(T)$ is the standard chemical potential of species $i$ at 1 atm pressure and temperature $T$ (in K).
$K_j$ is a function of temperature according to the Van’t Hoff equation:

$$\frac{d \ln K(T)}{dT} = \frac{\Delta H^0(T)}{RT^2} \tag{3}$$

where $\Delta H^0(T)$ is the enthalpy change of the reaction at temperature $T$ (Denbigh, 1981). For a small temperature range, $\Delta H^0(T)$ can be approximated by:

$$\Delta H^0(T) = \Delta H^0(T_0) + \Delta c_p^0(T - T_0) \tag{4}$$

where $\Delta c_p^0(T)$ is the change of molar heat capacity of products minus reactants. By substituting Eq. (4) into Eq. (3) and integrating from a reference temperature $T_0$ (typically at 298.15 K) to $T$, we obtain:

$$K(T) = K_0 \exp \left[ -\frac{\Delta H^0(T_0)}{RT_0} \left( \frac{T_0}{T} - 1 \right) - \frac{\Delta c_p^0}{R} \left( 1 + \ln \left( \frac{T_0}{T} \right) - \frac{T_0}{T} \right) \right] \tag{5}$$

where $K_0$ is the equilibrium constant at $T_0$.

2.2 Activity of species

The activity of species $i$, $a_i$, if an ideal gas, is equal to its partial pressure ($a_i = p_i$) (Seinfeld and Pandis, 1998). If $i$ is an electrolyte dissolved in water, $a_i = \gamma_i (\nu_+ + \nu_-) m_+ m_-^{\nu_+/\nu_-}$, where $\gamma_i$ is the activity coefficient of $i$ in water, $\nu_+$ and $\nu_-$ are the moles of cations and anions, respectively, released per mole of electrolyte and $m_+$, $m_-$ are their molalities, respectively. The activity of each solid phase species is assumed to be unity.

2.3 Activity coefficients

In ISORROPIA II, the multicomponent activity coefficients, $\gamma_{12}$ for each ionic pair 1–2 are computed using Bromley’s formula (Bromley, 1973),

$$\log \gamma_{12} = -A_y \frac{z_1 z_2 I^{1/2}}{1 + I^{1/2}} + \frac{z_1 z_2}{z_1 + z_2} \left[ \frac{F_1}{z_1} + \frac{F_2}{z_2} \right] \tag{6}$$
where $\gamma_{12}$ is the mean activity coefficient of cation 1 and anion 2 at 298.15 K, $A_y$ is the Debye-Hückel constant (0.511 kg$^{0.5}$ mol$^{-0.5}$ at 298.15 K) and,

$$F_1 = Y_{21} \log \gamma_{12}^o + Y_{41} \log \gamma_{14}^o + Y_{61} \log \gamma_{16}^o + \ldots + \frac{A_y I^{1/2}}{1 + I^{1/2}} [z_1 z_2 Y_{21} + z_1 z_4 Y_{41} + z_1 z_6 Y_{61} + \ldots]$$  \hspace{1cm} (7)

$$F_2 = X_{12} \log \gamma_{12}^o + X_{32} \log \gamma_{32}^o + X_{52} \log \gamma_{52}^o + \ldots + \frac{A_y I^{1/2}}{1 + I^{1/2}} [z_1 z_2 X_{12} + z_3 z_2 X_{32} + z_5 z_2 X_{52} + \ldots]$$  \hspace{1cm} (8)

where odd subscripts refer to cations and even subscripts refer to anions, $Y_{21} = \left( \frac{z_1 + z_2}{2} \right)^2 \frac{m_2}{I}$, $X_{12} = \left( \frac{z_1 + z_2}{2} \right)^2 \frac{m_1}{I}$, $z_i$ is the absolute charge of ionic species $i$, and $\gamma_{ij}^o$ is the mean ionic activity coefficient of the binary pair $i−j$ (“binary” activity coefficient) computed at the ionic strength of the multicomponent solution, $I$, $I = \frac{1}{2} \sum m_i z_i^2$.

Following the recommendations of Kim et al. (1993), binary activity coefficients, $\gamma_{12}^o$, are calculated using the Kusik-Meissner relationship (Kusik and Meissner, 1978),

$$\log \gamma_{12}^o = z_1 z_2 \log \Gamma^o$$  \hspace{1cm} (9)

where

$$\Gamma^o = [1 + B (1 + 0.1I)^q - B] \Gamma^*$$  \hspace{1cm} (10)

$$B = 0.75 - 0.065q$$  \hspace{1cm} (11)

$$\log \Gamma^* = \frac{-0.5107 I^{1/2}}{1 + C I^{1/2}}$$  \hspace{1cm} (12)

$$C = 1 + 0.055q \exp \left( -0.023I^3 \right)$$  \hspace{1cm} (13)

and $q$ is a parameter specific for each binary pair (Table 4).
The effect of temperature on multicomponent activity coefficients is described by (Meissner and Peppas, 1973):

$$\log \gamma_{ij}(T) = [1.125 - 0.005(T - 273.15)] \log \gamma_{ij}(T_0) - [0.125 - 0.005(T - 273.15)] A$$  \hspace{1cm} (14)

where \( \gamma_{ij}(T) \) is the multicomponent activity coefficient of the ionic pair i-j at temperature \( T \), and, \( A = - \frac{0.41}{1 + 0.5} + 0.039/0.92 \).

2.4 Aerosol water content

During the calculation of aerosol water content, it is assumed that the ambient water vapor pressure is unaffected by the aerosol water uptake (Seinfeld and Pandis, 1998). Therefore, if ambient relative humidity is known, phase equilibrium between gas and aerosol-phase (Seinfeld and Pandis, 1998) gives that the water activity, \( a_w \), is equal to the ambient fractional relative humidity, RH, (i.e., expressed on a 0.0 to 1.0 scale):

$$a_w = RH$$  \hspace{1cm} (15)

Instead of determining water content that satisfies the constraint of Eq. (15) from explicit calculations of water activity (which would require an iterative, hence computationally expensive procedure, (Stelson and Seinfeld, [1982])), the water uptake of aerosols is approximated through the ZSR relationship (Robinson and Stokes, 1965),

$$W = \sum_i \frac{M_i}{m_{oi}(a_w)}$$  \hspace{1cm} (16)

where \( W \) is the mass concentration of aerosol water (kg m\(^{-3}\) air), \( M_i \) is the molar concentration of species \( i \) (mol m\(^{-3}\) air), and \( m_{oi}(a_w) \) is the molality of an aqueous binary solution of the \( i \)-th electrolyte with the same \( a_w \) (i.e., relative humidity) as in the multicomponent solution. The water activities used and their corresponding sources are given in Table 6.
2.5 Deliquescence relative humidity (DRH)

For each salt, there is a characteristic relative humidity, known as the deliquescence relative humidity (DRH), above which a phase transition from solid to saturated aqueous solution occurs. The DRH varies with temperature and for small $T$ changes is given by (Wexler and Seinfeld, 1991):

$$\ln \frac{DRH(T)}{DRH(T_o)} = -\frac{M_w m_s L_s}{1000 R} \left( \frac{1}{T} - \frac{1}{T_o} \right)$$

(17)

where $M_w$ is the molar mass of water and $m_s$ is the molality of the saturated solution at temperature $T_o$. $L_s$ is the latent heat of fusion for the salt from a saturated solution given by $L_s = \Delta H_{cr} - \Delta H_{aq}$; $\Delta H_{cr}$, $\Delta H_{aq}$ are the molar enthalpies of formation of the crystalline phase and the species in aqueous solution, respectively.

2.6 Mutual deliquescence relative humidity (MDRH)

In every multicomponent mixture there exists a characteristic relative humidity (known as mutual deliquescence relative humidity, MDRH, Wexler and Seinfeld, 1991), for which all salts are saturated with respect to their aqueous solution. The MDRH is a eutectic point so it is below the DRH of all the pure solids composing the system and is the minimum RH for which a stable aqueous phase exists (Wexler and Seinfeld, 1991). When $\text{MDRH} < \text{RH} < \text{RH}_{\text{wet}}$ (where $\text{RH}_{\text{wet}}$ is the DRH of the salt with the lowest DRH in the mixture under consideration) the solution is said to be in the mutual deliquescence region (MDR, Nenes et al., 1998). Computing the aerosol composition in the MDR is a computationally demanding task (e.g., Potukuchi and Wexler, 1995a, b) which we seek to avoid. Given that the MDR corresponds usually to a narrow RH range, we approximate composition in a MDR using the Nenes et al. (1998) method, which involves computing the weighted average of a “dry” and “wet” solution:

$$W = (1 - c) W_{\text{wet}}$$

(18)
\[ G = cG_{\text{dry}} + (1 - c)G_{\text{wet}} \]  
\[ S = cS_{\text{dry}} + (1 - c)S_{\text{wet}} \]  
\[ D = (1 - c)D_{\text{wet}} \]  

The weighting factor, \( c \), is given by (Nenes et al., 1998):

\[ c = \frac{\text{RH} - \text{RH}_{\text{wet}}}{\text{MDRH} - \text{RH}_{\text{wet}}} \]  

and \( G, S, D \) are the concentrations of gaseous, solid and dissolved species, respectively. The subscripts “wet” and “dry” in Eqs. (18)–(22) denote the two solutions which are weighted. In the above equations, we assume that gases and solids are linearly weighted according to their proximity to \( \text{RH}_{\text{wet}} \) and MDRH (as expressed by \( c \)), while dissolved species are scaled to the amount of water. MDRH points for the new mixtures in ISORROPIA II are shown in Table 5. Although Eqs. (18)–(22) are an approximation of the thermodynamic solution, they qualitatively follow the RH-dependence of speciation and conserve aerosol dry mass.

3 ISORROPIA II: species considered and general solution procedure

The system modeled by ISORROPIA II consists of the following potential components (species in bold are new in ISORROPIA II):

- Gas phase: \( \text{NH}_3, \text{HNO}_3, \text{HCl}, \text{H}_2\text{O} \)
- Liquid phase: \( \text{NH}_4^+, \text{Na}^+, \text{H}^+, \text{Cl}^-, \text{NO}_3^-, \text{SO}_4^{2-}, \text{HNO}_3\text{(aq)}, \text{NH}_3\text{(aq)}, \text{HCl}\text{(aq)}, \text{HSO}_4^-\), \( \text{OH}^-\), \( \text{H}_2\text{O}, \text{Ca}^{2+}, \text{K}^+, \text{Mg}^{2+} \)
- Solid phase: \( (\text{NH}_4)_2\text{SO}_4, \text{NH}_4\text{HSO}_4, (\text{NH}_4)_3\text{H(SO}_4)_2, \text{NH}_4\text{NO}_3, \text{NH}_4\text{Cl}, \text{NaCl}, \text{NaNO}_3, \text{NaHSO}_4, \text{Na}_2\text{SO}_4, \text{CaSO}_4, \text{Ca(NO}_3)_2, \text{CaCl}_2, \text{K}_2\text{SO}_4, \text{KHSO}_4, \text{KNO}_3, \text{KCl}, \text{MgSO}_4, \text{Mg(NO}_3)_2, \text{MgCl}_2 \)
Table 1 shows thermodynamic properties for all species considered. Table 2 displays all the equilibrium reactions used in ISORROPIA II along with values for their equilibrium constants. When the concentration of crustals (Ca, K, Mg) is zero, routines of ISORROPIA are used, which since its original release (Nenes et al., 1998) has been substantially improved for robustness, speed and expanded to solve a wider range of problems (updates can be obtained from http://nenes.eas.gatech.edu/ISORROPIA).

3.1 Solution procedure

The number of species and equilibrium reactions is determined by the relative abundance of each aerosol precursor (NH₃, Na, Ca, K, Mg, HNO₃, HCl, H₂SO₄) and the ambient relative humidity and temperature. The major species potentially present are determined from the value of the following ratios:

\[
R_1 = \frac{[\text{NH}_4^+] + [\text{Ca}^{2+}] + [\text{K}^+] + [\text{Mg}^{2+}] + [\text{Na}^+]}{[\text{SO}_4^{-2}]}
\]

\[
R_2 = \frac{[\text{Ca}^{2+}] + [\text{K}^+] + [\text{Mg}^{2+}] + [\text{Na}^+]}{[\text{SO}_4^{-2}]}
\]

\[
R_3 = \frac{[\text{Ca}^{2+}] + [\text{K}^+] + [\text{Mg}^{2+}]}{[\text{SO}_4^{-2}]}
\]

where \([X]\) denotes the concentration of an aerosol precursor \(X\) (mol m\(^{-3}\) of air). \(R_1, R_2\) and \(R_3\) are termed “total sulfate ratio”, “crustals and sodium ratio” and “crustals ratio” respectively; based on their values, 5 aerosol composition regimes are defined, the possible species for which are listed in Table 3.
The DRH at $T_o=298.15$ K, the thermodynamic data for the $L_s$ (Eq. 17) as well as the Kussik-Meissner activity coefficient parameters (Eq. 13) are shown in Table 4. Table 6 displays the polynomial fit parameters for computing the molalities of binary solutions as a function of water activity (obtained from Kim and Seinfeld, 1995; Ha and Chan, 1999; and Kelly and Wexler, 2006) for CaSO$_4$, Ca(NO$_3$)$_2$, CaCl$_2$, K$_2$SO$_4$, KHSO$_4$, KNO$_3$, KCl, MgSO$_4$, Mg(NO$_3$)$_2$ and MgCl$_2$. For (NH$_4$)$_2$SO$_4$, NH$_4$HSO$_4$, (NH$_4$)$_3$H(SO$_4$)$_2$, NH$_4$NO$_3$, NH$_4$Cl, NaCl, NaNO$_3$, NaHSO$_4$ and Na$_2$SO$_4$, the water activity database was updated since the original release of ISORROPIA, using the output from the AIM model [http://www.hpc1.uea.ac.uk/~e770/aim.html](http://www.hpc1.uea.ac.uk/~e770/aim.html).

As in ISORROPIA, ISORROPIA II solves two classes of problems:

1. Forward (or “closed”) problems, in which known quantities are $T$, RH and the total (gas + aerosol) concentrations of NH$_3$, H$_2$SO$_4$, Na, HCl, HNO$_3$, Ca, K, and Mg.

2. Reverse (or “open”) problems, in which known quantities are $T$, RH and the precursor concentrations of NH$_3$, H$_2$SO$_4$, Na, HCl, HNO$_3$, Ca, K, and Mg in the aerosol phase.

Below the MDRH of an aerosol mixture, the particle is a solid if the aerosol is following its deliquescence branch. However, when the RH over a wet particle is decreasing, the wet aerosol may not crystallize below the MDRH but instead remain in a metastable state, where it is composed of an aqueous supersaturated solution (Seinfeld and Pandis, 1998). ISORROPIA II can address both states (termed “stable” where salts precipitate once the aqueous phase becomes saturated with respect to them, and, “metastable”, if the aerosol is composed only of an aqueous phase which can be supersaturated with respect to dissolve salts).

Depending on the three sulfate ratios and the relative humidity, ISORROPIA II solves the appropriate set of equilibrium equations and together with mass conservation, electroneutrality, water activity equations and activity coefficient calculations, the final concentrations at thermodynamic equilibrium are obtained. Figure 1 illustrates a general description of the solution procedure.
3.2 Important issues

- When calculating species concentration, the stable state solution algorithm of ISORROPIA II starts with assuming a completely dry aerosol. As the ambient relative humidity increases (or decreases) ISORROPIA II dissolves each of the salts present (depending on their DRH) and calculates solid and ion concentrations and water uptake. The exact opposite methodology is adopted by other models. For example, SCAPE2 initially assumes that all salts present are completely dissolved and based on the ambient relative humidity and DRH of each salt calculates solid concentration if a precipitate is assumed to form. Differences in the “solution dynamics” may lead to differences in water content and speciation, especially at low RH, and are further analyzed in Sect. 4.

- ISORROPIA II uses the principle of “compositional invariance with RH cycling” to determine the aerosol composition at low RH (i.e., when the aerosol is solid). This is done because aerosol cycles RH many times in nature throughout its lifetime and the invariant solution will in general represent its composition more accurately in the atmosphere. Compositional invariance is applied when the aerosol contains volatile anions, sulfate and non-volatile univalent cations (Na, K). In such cases, Na and K preferentially associate with SO₄ to form Na₂SO₄ and K₂SO₄ before they are bound with NO₃ and Cl to form NaNO₃, KNO₃, NaCl, and KCl. Other models may not adopt this approach and may lead to differences in predicted water uptake, especially at low RH. For example, ISORROPIA II predicts that potassium will preferentially neutralize sulfate to form K₂SO₄. Then excess potassium reacts with available HNO₃ and HCl to form KNO₃ and KCl. Therefore, in the above example ISORROPIA II assumes that potassium mainly binds with sulfate since sulfate is less volatile than nitrate or chloride when exposed to RH cycling, thus more likely to stay in the aerosol phase and form K₂SO₄.
3.3 Simplifications and assumptions in ISORROPIA II

Numerous simplifying assumptions are taken to increase computational speed and numerical stability without compromising rigor substantially. These are:

- Sulfuric acid, sodium and crustals have a very low vapor pressure and can safely be assumed that they exclusively reside in the aerosol phase.

- The first dissociation of sulfuric acid \( \left( H_2SO_4(aq) \rightarrow H^+ + HSO_4^- \right) \) is assumed to be complete and not considered in the equilibrium calculations.

- For a wide range of ionic strengths (0–30 M), typical of ambient aerosols, the solubility product of magnesium sulfate (MgSO_4) was found to be always less than its equilibrium constant. Therefore, ISORROPIA II assumes MgSO_4 is always deliquesced when an aqueous phase is present, avoiding any computations for precipitating MgSO_4 out of solution.

- Calcium sulfate (CaSO_4) is assumed completely insoluble.

- For sulfate rich cases \( (R_1 < 2) \) NH_3(g), NO_3^-(aq) and Cl^-(aq) are assumed minor species that do not significantly perturb the equilibrium through the \( NH_3(g) + H_2O(aq) \leftrightarrow NH_4^+(aq) + OH^-(aq) \), HNO_3(g) ↔ H^+(aq) + NO_3^-(aq) and HCl(g) ↔ H^+(aq) + Cl^-(aq) reactions, respectively. The code solves the appropriate set of equilibrium reactions (for the major species) and then the three gases (NH_3(g), HNO_3(g), HCl(g)) are subsequently dissolved through the equilibria described above. The same is assumed for the dissolved undissociated ammonia, nitric and hydrochloric acid in the aqueous phase (NH_3(aq), HNO_3(aq), HCl(aq)).

- For sulfate poor cases \( (R_1 > 2) \) bisulfate ion \( (HSO_4^-) \) is considered a minor species from the reaction \( HSO_4^- (aq) \leftrightarrow H^+ (aq) + SO_4^{2-} (aq) \) (see Table 3).
MDRH points for multicomponent mixtures containing crustals are not known; They are approximated instead with data for known mixtures with as similar as possible composition (Table 5). For example, the MDRH point for a (NH$_4$)$_2$SO$_4$–NH$_4$NO$_3$–NH$_4$Cl–Na$_2$SO$_4$–K$_2$SO$_4$–MgSO$_4$ mixture is (not known and) assumed to be the same as for the (NH$_4$)$_2$SO$_4$–NH$_4$NO$_3$–NH$_4$Cl–Na$_2$SO$_4$ mixture. The absence of crustals in the consideration of the MDRH points of those mixtures is expected to introduce small underprediction of water, since i) both potassium and magnesium have similar deliquescence properties with sodium (Moya et al., 2001a), and, ii) highly insoluble salts (i.e., CaSO$_4$) do not significantly impact water activity, hence do not significantly contribute to DRH depression.

– OH$^-$ is assumed a minor species.

– When crustals are in excess compared to all the anions, ISORROPIA II assumes that the solution is close to neutral (pH≈7). This is consistent with a presence of excess carbonate in the aerosol phase, which has a pK$_a$ of ~6.4 (Meng et al., 1995).

– The DRH of NH$_4$NO$_3$ is strongly dependent on temperature. Under low temperature conditions (T<270 K), this changes the order (starting from low to high RH) with which salts deliquesce (Fig. 2). For these cases the DRH of NH$_4$NO$_3$ in ISORROPIA II is assumed to not “cross over” the DRH of the other salts present in the solution, especially since thermodynamic data for supercooled NH$_4$NO$_3$ solutions are not known. The same is assumed for NH$_4$Cl and NaNO$_3$ which exhibit similar behavior with NH$_4$NO$_3$ (Fig. 2).

– $\gamma_{\text{OH}^-}$ and $\gamma_{H^+}$ are assumed equal to unity, as the activity coefficient routines cannot explicitly calculate them.
3.4 ISORROPIA II: new features

The main improvements to the original ISORROPIA release (Nenes et al., 1998) which are included in ISORROPIA II (and in the latest release of ISORROPIA version 1.7, http://nenes.eas.gatech.edu/ISORROPIA) are:

- Gas/liquid/solid partitioning has been extended to include crustal elements which resulted in 10 more salts in the solid phase and 3 more ions in the aqueous phase (Table 3).

- In addition to a thermodynamically stable state the aerosol can also be in a metastable state where no precipitate is formed (always an aqueous solution).

- The water activity database has been updated, using the output from the AIM model (http://www.hpc1.uea.ac.uk/~e770/aim.html).

- Temperature dependency of the activity coefficients is included. This has been done for both pre-calculated tables and online calculations of activity coefficients.

- The MDRH points for all the systems considered have been calculated using the GFEMN model of Ansari and Pandis (1999b).

- The activity coefficient calculation algorithm has been optimized to increase computational speed and avoid numerical errors.

- The tabulated Kusik-Meissner binary activity coefficient data have been recomputed through the online calculations for the midpoint of each ionic strength interval.

- A new subroutine has been added to provide the user with the option to “force” ISORROPIA II to conserve mass up to machine precision.
4 Evaluation of ISORROPIA II

ISORROPIA II is evaluated against the predictions of SCAPE2 for a wide range of conditions characteristic of urban, remote continental, non-urban continental and marine aerosol (Heitzenberg, 1989; Fitzgerald, 1991; Ansari and Pandis, 1999a). For urban and non-urban continental aerosol, sulfates, nitrates and ammonium are usually dominant inorganic species. Sodium and chloride often compose the majority of the marine particulate matter (usually with some crustals and sulfates present). This classification is mainly qualitative, as mixing between aerosol types often occurs in the atmosphere.

Table 7 lists the 16 different sets of precursor concentrations that were used in the intercomparison study. Sulfuric acid concentrations range between $1.0-5.7 \mu g m^{-3}$ for marine and non-urban continental and $10.0-15.0 \mu g m^{-3}$ for urban and remote continental aerosol. For the 16 cases considered, conditions 3, 4, 15 and 16 are sulfate-rich ($R_1<1$ or $1<R_1<2$), conditions 1, 2, 13 and 14 represent sulfate near-neutral ($R_1 \approx 2$) aerosol and cases 5–12 are sulfate-poor ($R_1>2$), (Table 7). For each set of precursor concentrations, composition at thermodynamic equilibrium was calculated for 11 different RHs ranging from 10–98%; temperature was kept fixed at 298.15 K. In the evaluation study both the thermodynamically stable and metastable state solutions of ISORROPIA II are computed.

For the intercomparison study we calculate the normalized mean error (NME) defined as $NME = \frac{1}{n} \sum_{i} \left| I_i - S_i \right|$, where $I_i$ represents predictions of ISORROPIA II for case $i$, $S_i$ predictions of SCAPE2 and $n$ is the total number of cases considered.

Finally we compare the CPU time requirements between SCAPE2 and ISORROPIA II, stable and metastable solution of ISORROPIA II, as well as between ISORROPIA II and ISORROPIA for all the simulation conditions of Table 7.
4.1 Overall assessment of ISORROPIA II vs. SCAPE2

For all the simulations performed in this work, the water activity database of SCAPE2 was replaced with the one used in ISORROPIA II (reflecting the most updated water activity database). Activities of aqueous species in SCAPE2 were computed using Bromley’s formula for multicomponent activity coefficients and the Kussik-Meissner method for binary coefficients.

In Fig. 3 we compare predictions of aerosol water, nitrate, chloride, ammonium, total PM and hydrogen concentrations between ISORROPIA II (stable solution, forward problem solved), and SCAPE2 for the conditions specified in Table 7. Both models predict similar amount of aerosol water content (Fig. 3a) with a normalized mean error of 13.5%. Most of this discrepancy is found in the low RH regimes (RH<60%) where SCAPE2 predicts higher water concentration compared to ISORROPIA II. This discrepancy is attributed to a) non-convergence of SCAPE2, which is corroborated by the large CPU time required for obtaining a solution (see Table 9), and, b) errors in the calculations of activity coefficients (both binary and multicomponent). At low RH (i.e., low liquid water content), the aqueous solution is highly non-ideal (hence the solution highly non-linear), consequently small changes in activity coefficients may result in large changes in the dissolved species concentrations and the predictions of liquid water content. A few cases exist (for RH>65%) for which ISORROPIA II predicts less aerosol water than SCAPE2 (Fig. 3a); this originates from differences in aerosol nitrate which then affects water uptake. For a few marine cases, SCAPE2 predicts negligible water due to non-convergence (Fig. 3a).

In Fig. 3b, total aerosol nitrate concentrations are compared for all the input conditions of Table 7. Overall, the agreement is very good with a mean error of 16.5%. ISORROPIA II predicts non-negligible amount of nitrate for some urban cases while SCAPE2 does not. For a few non-urban continental cases ISORROPIA II underpredicts aerosol nitrate compared to SCAPE2. The sources of these discrepancies are further investigated through specific examples in Sect. 4.2.
Aerosol chloride concentration predictions are shown in Fig. 3c where both models show similar results (NME=6.5%) with small discrepancies for a few marine cases (due to non-convergence of SCAPE2 solution) in which chloride exists in significant amount due to significant presence of sea salt particles.

For aerosol ammonium predictions (Fig. 3d), no substantial differences between the two models were found (NME=2.1%). Discrepancies were primarily found in some non-urban continental cases which represent a sulfate-poor, ammonium-rich environment and are further analyzed in Sect. 4.2. Even though a few differences exist in the predicted concentrations of semi-volatile species, the total PM composition (Fig. 3e) shows very good agreement (NME=13.0%). The worst agreement between the two models was seen for H⁺ predictions (Fig. 3f) with the normalized mean error significantly higher than for any other component (NME=64%). The discrepancy occurs at low RH (as it scales with water content).

SCAPE2 predictions are also compared against the metastable state solution of ISORROPIA II (Fig. 4). Table 8 shows normalized mean errors between ISORROPIA II (both stable and metastable solutions) and SCAPE2 for the simulations of Table 7. As can be seen in Figs. 3, 4 and Table 8, the stable state predictions of ISORROPIA II are closer to SCAPE2 predictions. This is expected since for low RHs (<40%) SCAPE2 solution, by always attempting to solve for a liquid phase, deviates from the stable state behavior, moving towards the metastable state (see Sect. 3.2).

4.2 Understanding the discrepancies between ISORROPIA II and SCAPE2

The previous discussion provides an overall intercomparison of the two models for a broad RH and composition domain; some cases are further examined to gain more insight as to the cause of discrepancies. In Fig. 5 we compare aerosol water content, aqueous phase potassium, aqueous phase ammonium and aqueous phase nitrate concentration predictions for case 3 (see Table 7) which produced the largest discrepancy in aerosol water and total PM concentrations. This case represents an urban type aerosol with the solution being highly acidic ($R_1=1.27$). Under such conditions, the wa-
ter content discrepancy between the models is largest for low RHs for the reasons outlined in Sect. 3.2. This is clearly shown in Fig. 5a where only for RH>70% SCAPE2 and ISORROPIA II closely follow each other. SCAPE2 predicts significant amount of aqueous phase potassium (Fig. 5b) and ammonium (Fig. 5c) at low relative humidities, while ISORROPIA II predicts gradual deliquescence of K$_2$SO$_4$ from 65% to 85% RH. However, SCAPE2 predicts complete deliquescence of K$_2$SO$_4$ at RH=55% which may be due to non-convergence of its numerical solution. Particulate phase ammonium is mainly present as ammonium bisulfate (NH$_4$HSO$_4$) and letovicite ((NH$_4$)$_3$(H(SO$_4$)$_2$) in ISORROPIA II. However, SCAPE2 predicts the formation of (NH$_4$)$_3$H(SO$_4$)$_2$ only, throughout the whole RH regime. This can also be seen in Fig. 5c where ISORROPIA II predicts a two-step dissolution of ammonium; one at RH=40% from the deliquescence of (NH$_4$)$_3$H(SO$_4$)$_2$ and one at RH=70% from the deliquescence of NH$_4$HSO$_4$. Water uptake with SCAPE2 exhibits deliquescence only of (NH$_4$)$_3$H(SO$_4$)$_2$ at RH=40%. Both models predict similar amounts of aqueous phase nitrate for all RHs (Fig. 5d) which shows that the assumption of ISORROPIA II for NO$_3$$_{aq}$ being a minor species for sulfate – rich cases is a good assumption.

Figure 6 shows comparison of aerosol water, NaCl$_{(s)}$ and K$_{(aq)}$ and Mg$_{(aq)}$ predictions for case 12 (see Table 7), which is a sulfate poor, sodium and crustal species rich aerosol ($R_1$=5.1). The two models agree well (mean error of 5.1%) in aerosol water content predictions (Fig. 6a). SCAPE2, however, predicts significantly higher aqueous potassium for RH<40% (Fig. 6b). This is mainly due to different approaches used to associate K with NO$_3^-$ and SO$_4^{2-}$ at low RH. ISORROPIA II uses the principle of “compositional invariance” (Sect. 3.2), hence it preferentially associates K with SO$_4^{2-}$ to form K$_2$SO$_4$, and then KNO$_3$ and KCl. SCAPE2 tends to partition first as KNO$_3$ and KCl and then as K$_2$SO$_4$. Since the DRH of KCl is lower than K$_2$SO$_4$, SCAPE2 deliquesces aerosol potassium at a lower RH than ISORROPIA II. Unlike potassium, both models predict the partitioning of sodium between sodium nitrate (NaNO$_3$) and sodium chloride (NaCl) in a similar way. This is shown in Fig. 6c where the dissociation of NaCl$_{(s)}$ as a function of RH is similar between both models (NME=12.1%). Aqueous
magnesium is the same in both models (Fig. 6d), supporting the postulation (Sect. 3.3) that MgSO$_4$ never precipitates out of solution.

In Fig. 7 we compare aerosol water, NO$_3$(aq) and NH$_4$(aq) as a function of RH for case 5, a sulfate poor, ammonium rich aerosol ($R_1=23.9$, $R_2=0.80$, $R_3=0.37$). Compared to SCAPE2, ISORROPIA II slightly underpredicts aerosol water, aqueous nitrate and ammonium. This difference is seen for RHs between 25–65%. That is because SCAPE2 predicts total deliquescence of sulfates at RH=40% while ISORROPIA II does at RH=70%. The increase of water content shifts the equilibrium of HNO$_3(g) \leftrightarrow H^+(aq) + NO_3^-(aq)$ and NH$_3(g) + H_2O(aq) \leftrightarrow NH_4^+(aq) + OH^-(aq)$ to the right predicting more aqueous nitrate (Fig. 7b) and ammonium (Fig. 6c) for the same RH regime.

4.3 Metastable vs. stable solutions

The differences between metastable and stable thermodynamic solutions of ISORROPIA II are illustrated in Fig. 8; SCAPE2 is also included for comparison. Figure 8 shows aerosol water and aqueous potassium concentration as a function of relative humidity for a sulfate near-neutral aerosol (case 13 of Table 7). The thermodynamically stable solution of ISORROPIA II predicts deliquescence of the aerosol mixture at 60% RH (DRH of ammonium nitrate). The MDRH for this specific aerosol mixture is 0.46, which explains the aqueous phase potassium (and aerosol water) concentration predicted by the deliquescence solution of ISORROPIA II between 40 and 60% RH. As expected, the metastable solution predicts significant amounts of water below the MDRH (and by definition particulate potassium is deliquesced at all RHs). SCAPE2 yields a solution that is between the stable and metastable ISORROPIA II. Below 40% RH, the predicted concentration of aerosol water by SCAPE2 is slightly larger than the stable solution of ISORROPIA II (Fig. 8a). This results in partial dissolution of aerosol potassium (RH<40%) predicted by SCAPE2 as opposed to the stable solution of ISORROPIA II which does not predict deliquescence of aerosol potassium for this RH regime (Fig. 8b).
4.4 “Forward” vs. “Reverse” problem solution

ISORROPIA II is designed to solve both forward and reverse problems. It is useful to assess whether the two solution modes predict identical outputs for the same input. For this assessment, the output from the forward problem (particulate phase concentrations of NH₄, SO₄, Na, Cl, NO₃, Ca, K, and Mg) has been used as input to the reverse problem. The two solution modes are assessed by comparing predictions of aqueous nitrate and sulfate. Since sulfate is only found in the aerosol phase, aqueous phase sulfate calculations are used to evaluate the solid/liquid partitioning behavior between the two solution algorithms, while aqueous nitrate is used as a proxy for gas-aerosol partitioning (for all the conditions specified in Table 7). The agreement between the two solutions was found to be excellent with the NME being 3.4±1.1% for aqueous sulfate and 2.5±1.3% for aqueous nitrate concentration.

4.5 Computational speed

The timing tests were performed on a Dell 8300 Intel Pentium 4 CPU 3.20 GHz, 512 MB of RAM workstation running Windows XP operating system. Both codes were compiled with Watcom FORTRAN compiler version 2.0 with full optimization options on. Table 9 shows the CPU time needed by the two models for the aerosol types described in Table 7. ISORROPIA II consumes much less CPU time compared to SCAPE2 with the difference being at least an order of magnitude for all aerosol cases. The amount of time required by ISORROPIA II for each aerosol case was found to be approximately the same even if the convergence criterion for solids and water was decreased down to 10⁻⁶ or 10⁻⁷ which is a proof of the rapid and robust convergence of the code. However, larger convergence criterion was used for the intercomparison study (see Table 9), to assure a quick and convergent solution from SCAPE2. For completeness we also compare the CPU time required by ISORROPIA (version 1.7, 03/15/2006) for all the simulation conditions of Table 7, but with crustals set to zero). Although ISORROPIA II solves for more species than ISORROPIA, it is not slower because of
optimizations in the activity coefficient calculation algorithm in ISORROPIA II. Finally, in Table 9 we compare the CPU time required by the stable and metastable solutions of ISORROPIA II. As expected, the metastable solution is slightly faster than the stable solution since the absence of solid species requires the solution of fewer equations.

5 Summary

A new model, ISORROPIA II, is developed which treats the thermodynamics of $\text{K}^+ - \text{Ca}^{2+} - \text{Mg}^{2+} - \text{NH}_4^+ - \text{Na}^+ - \text{SO}_4^{2-} - \text{NO}_3^- - \text{Cl}^- - \text{H}_2\text{O}$ aerosol systems. A comprehensive evaluation was conducted against the thermodynamic model SCAPE2 in terms of composition predicted and computational speed for a wide variety of aerosol conditions that cover typical urban, remote continental, marine and non-urban continental environments. The overall predictions of aerosol water, total PM and concentration of semi-volatile species were generally comparable between the two models under most conditions. For aerosol water content and total PM mass the two models agreed within approximately 13%. The normalized mean error for total aerosol nitrate predictions was 16% while for aerosol chloride and ammonium concentration the agreement was within 2–6%. Small discrepancies were found to exist between the two models under certain conditions, primarily for relative humidities between 40 and 70%. These discrepancies are mainly attributed to the solution dynamics treatment of water uptake in mutual deliquescence regions and the association of non-volatile cations with sulfate, nitrate and chloride. For all cases examined, ISORROPIA II is more than an order of magnitude faster than SCAPE2, showing robust and rapid convergence for all conditions examined, making it one of the most computationally efficient and comprehensive inorganic thermodynamic equilibrium modules available.

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Table 1. Thermodynamic Properties for all species in ISORROPIA II∗.

| Species       | $\Delta \mu^0$ (298K), kJ mol$^{-1}$ | $\Delta H^0$ (298K), kJ mol$^{-1}$ | $C^0$, J mol$^{-1}$ K$^{-1}$ |
|---------------|--------------------------------------|-------------------------------------|-------------------------------|
| Ca(NO$_3$)$_2$(s) | -743.070                             | -938.390                           | 149.370                       |
| CaCl$_2$(s)    | -748.10                              | -795.800                           | 72.590                        |
| CaSO$_4$(s)    | -1798.280                            | -2022.630                          | 186.020                       |
| KHSO$_4$(s)    | -1031.300                            | -1160.600                          | 87.160                        |
| K$_2$SO$_4$(s) | -1321.370                            | -1437.790                          | 131.460                       |
| KNO$_3$(s)     | -394.860                             | -494.630                           | 96.400                        |
| KCl$_2$(s)     | -409.140                             | -434.750                           | 51.300                        |
| MgSO$_4$(s)    | -1170.600                            | -1284.900                          | 96.480                        |
| Mg(NO$_3$)$_2$(s) | -589.400                            | -790.650                           | 141.920                       |
| MgCl$_2$(s)    | -591.790                             | -641.320                           | 71.380                        |
| Ca(aq)         | -553.580                             | -542.830                           |                             |
| K$_2$(aq)      | -283.270                             | -252.380                           | 21.800                        |
| Mg$_2$(aq)     | -454.800                             | -466.850                           |                             |
| NaCl$_2$(s)    | -384.138                             | -411.153                           | 50.500                        |
| NaNO$_3$(s)    | -367.000                             | -467.850                           | 92.880                        |
| Na$_2$SO$_4$(s) | -1270.160                            | -1387.080                          | 128.200                       |
| NaHSO$_4$(s)   | -992.800                             | -1125.500                          | 85.000                        |
| NH$_4$Cl$_2$(s) | -202.870                             | -314.430                           | 84.100                        |
| NH$_4$NO$_3$(s) | -183.870                             | -365.560                           | 139.300                       |
| (NH$_4$)$_2$SO$_4$(s) | -901.670 | -1180.850 | 187.490          |
| NH$_4$HSO$_4$(s) | -823.000                            | -1026.960                          | 127.500                       |
| (NH$_4$)$_3$H(SO$_4$)$_2$(s) | -1730.000 | -2207.000 | 315.000          |
| HNO$_3$(g)     | -74.720                              | -135.060                           | 53.350                        |
| HCl$_2$(g)     | -95.299                              | -92.307                            | 29.126                        |
| NH$_3$(g)      | -16.450                              | -46.110                            | 35.060                        |
| NH$_3$(aq)     | -26.500                              | -80.290                            | 79.900                        |
| H$_2$(aq)      | 0.000                                | 0.000                              | 0.000                         |
| NO$_2$(aq)     | -261.905                             | -240.120                           | 46.400                        |
| NH$_2$(aq)     | -79.310                              | -132.510                           | 79.900                        |
| HSO$_4$(aq)    | -755.910                             | -887.340                           | -84.000                       |
| SO$_4^2$ (aq)  | -744.530                             | -909.270                           | -293.000                      |
| NO$_3$(aq)     | -111.250                             | -207.360                           | -86.600                       |
| Cl$_2$(aq)     | -131.228                             | -167.159                           | -136.400                      |
| OH$^-$ (aq)    | -157.244                             | -229.994                           | -148.500                      |

∗ Compiled by: Kim and Seinfeld, (1995), Kim et al., (1993); Species in bold are new in ISORROPIA II.

† Data not available.
Table 2. Equilibrium Relations and Temperature Dependence Constants used in ISORROPIA II∗.

| Reaction                              | Equilibrium Constant Expression | $K^0$ (298.15 K) | $\Delta H^0(T_0)$ | $\Delta S^0(T_0)$ | Units         |
|---------------------------------------|---------------------------------|------------------|------------------|------------------|---------------|
| Ca(NO$_3$)$_2$(aq) ↔ Ca$^{2+}$(aq) + 2NO$_3^-$ (aq) | $[\text{Ca}^{2+}]$ 2NO$_3^-$ | 6.067×10$^6$ | 9.549 | – | mol$^3$kg$^{-3}$ |
| CaCl$_2$(aq) ↔ Ca$^{2+}$(aq) + 2Cl$^-$ (aq) | $[\text{Ca}^{2+}]$ 2Cl$^-$ | 7.974×10$^{11}$ | 27.995 | – | mol$^3$kg$^{-3}$ |
| CaSO$_4$ 2H$_2$O (aq) ↔ Ca$^{2+}$(aq) + SO$_4^{2-}$ (aq) + 2H$_2$O | $[\text{Ca}^{2+}]$ SO$_4^{2-}$ | 4.319×10$^{-5}$ | – | – | mol$^2$kg$^{-2}$ |
| K$_2$SO$_4$(aq) ↔ 2K$^+$ + SO$_4^{2-}$ (aq) | $[K^+]^2$ SO$_4^{2-}$ | 1.569×10$^{-2}$ | –9.589 | 45.807 | mol$^3$kg$^{-3}$ |
| KHSO$_4$(aq) ↔ K$^+$ + HSO$_4^-$ (aq) | $[K^+]$ HSO$_4^-$ | 24.016 | –8.423 | 17.964 | mol$^2$kg$^{-2}$ |
| KNO$_3$(aq) ↔ K$^+$ + NO$_3^-$ (aq) | $[K^+]$ NO$_3^-$ | 0.872 | 14.075 | 19.388 | mol$^2$kg$^{-2}$ |
| KCl(aq) ↔ K$^+$ + Cl$^-$ (aq) | $[K^+]$ Cl$^-$ | 8.680 | –6.167 | 19.953 | mol$^2$kg$^{-2}$ |
| MgSO$_4$(aq) ↔ Mg$^{2+}$(aq) + SO$_4^{2-}$ (aq) | $[\text{Mg}^{2+}]$ SO$_4^{2-}$ | 1.079×10$^6$ | 36.798 | – | mol$^2$kg$^{-2}$ |
| Mg(NO$_3$)$_2$(aq) ↔ Mg$^{2+}$(aq) + 2NO$_3^-$ (aq) | $[\text{Mg}^{2+}]$ 2NO$_3^-$ | 2.507×10$^{15}$ | 36.677 | – | mol$^3$kg$^{-3}$ |
| MgCl$_2$(aq) ↔ Mg$^{2+}$(aq) + 2Cl$^-$ (aq) | $[\text{Mg}^{2+}]$ 2Cl$^-$ | 9.557×10$^{21}$ | 59.352 | – | mol$^3$kg$^{-3}$ |
| HSO$_4^{-}$(aq) ↔ H$^+$ + SO$_4^{2-}$ (aq) | [HSO$_4^-$] H$^+$ | 1.015×10$^{-2}$ | 8.85 | 25.14 | mol$^2$kg$^{-1}$ |
| NH$_3$(g) ↔ NH$_3$(aq) | [NH$_3$(aq)] NH$_3$(g) | 5.764×10$^1$ | 13.79 | –5.39 | mol$^{-1}$ atm$^{-1}$ |
| NH$_3$(aq)H$_2$O(aq) ↔ NH$_4^+$(aq) + OH$^-$ (aq) | [NH$_3$(aq)H$_2$O(aq)] NH$_4^+$ | 1.805×10$^{-15}$ | –1.50 | 26.92 | mol$^{-1}$ |
| HNO$_3$(g) ↔ H$^+$ + NO$_3^-$ (aq) | [HNO$_3$(g)] H$^+$ | 2.511×10$^6$ | 29.17 | 16.83 | mol$^2$kg$^{-2}$ atm$^{-1}$ |
| HNO$_2$(g) ↔ HNO$^*$ (aq) | [HNO$_2$(g)] HNO$^*$ | 2.1×10$^5$ | 29.17 | 16.83 | mol$^{-1}$ atm$^{-1}$ |
| HClO$^+$ (aq) + C$^-$ (aq) | [HClO$^+$ (aq)] C$^-$ | 1.971×10$^6$ | 30.20 | 19.91 | mol$^2$kg$^{-2}$ atm$^{-1}$ |
| HClO$^+$ (aq)H$^+$ (aq) | [HClO$^+$ (aq)H$^+$ (aq)] H$^+$ | 2.5×10$^3$ | 30.20 | 19.91 | mol$^{-1}$ atm$^{-1}$ |
| H$_2$O$^+$ (aq) + OH$^-$ (aq) | [H$_2$O$^+$ (aq) + OH$^-$ (aq)] H$^+$ | 1.010×10$^{-14}$ | –22.52 | 26.92 | mol$^2$kg$^{-2}$ |
Table 2. Continued.

| Reaction | Equilibrium Constant Expression | $K^0$ (298.15K) | $\Delta H^0 (T, R)$ | $\Delta S^0$ | Units |
|----------|---------------------------------|------------------|---------------------|-------------|-------|
| $Na_2SO_4^{2+} + 2Na_2^{+} + SO_4^{2-}$ | $[Na_2^{+}]^2 [SO_4^{2-}]$ | $4.799 \times 10^{-1}$ | 0.98 | 39.75 | $mol^3 kg^{-3}$ |
| $(NH_4)_2SO_4^{2+} + 2NH_4^{+} + SO_4^{2-}$ | $[NH_4^{+}]^2 [SO_4^{2-}]$ | $1.817 \times 10^0$ | $-2.65$ | 38.57 | $mol^3 kg^{-3}$ |
| $NH_4Cl_{(s)} \leftrightarrow NH_3(g) + Cl^{-}_{(aq)}$ | $K_{NH_4Cl}$ | $1.086 \times 10^{-16}$ | $-71.00$ | 2.40 | $atm^2$ |
| $NaNO_3_{(s)} \leftrightarrow Na^+_{(aq)} + NO_3^{-}_{(aq)}$ | $[Na^+] [NO_3^-]$ | $1.197 \times 10^1$ | $-8.22$ | 16.01 | $mol^2 kg^{-2}$ |
| $NaCl_{(s)} + Cl^{-}_{(aq)}$ | $[Na^+] [Cl^-]$ | $3.766 \times 10^1$ | $-1.56$ | 16.90 | $mol^2 kg^{-2}$ |
| $NaHSO_4_{(s)} \leftrightarrow Na^+_{(aq)} + HSO_4^{-}_{(aq)}$ | $[Na^+] [HSO_4^-]$ | $2.413 \times 10^4$ | 0.79 | 14.75 | $mol^2 kg^{-2}$ |
| $NH_4NO_3_{(s)} \leftrightarrow NH_3(g) + HNO_3(g)$ | $P_{NH_4NH_3}$ | $4.199 \times 10^{-17}$ | $-74.735$ | 6.025 | $atm^2$ |
| $NH_4HSO_4_{(s)} \leftrightarrow NH_4^+_{(aq)} + HSO_4^{-}_{(aq)}$ | $[NH_4^+] [HSO_4^-]$ | $1.383 \times 10^0$ | $-2.87$ | 15.83 | $mol^2 kg^{-2}$ |
| $(NH_4)_2SO_4_{(s)} \leftrightarrow 3NH_4^+_{(aq)} + SO_4^{2-}_{(aq)}$ | $[NH_4^+]^3 [SO_4^{2-}]$ | $2.972 \times 10^1$ | $-5.19$ | 54.40 | $mol^5 kg^{-5}$ |

* Compiled by: Kim and Seinfeld (1995), Kim et al. (1993); Reactions with constants in bold are new in ISORROPIA II.

* The equilibrium constant $K_{1b}$ of the reaction $HNO_3_{(aq)} \leftrightarrow H^+_{(aq)} + NO_3^-_{(aq)}$ is calculated from $K_1$ and $K_{1a}$ of the reactions $HNO_3_{(g)} \leftrightarrow H^+_{(aq)} + NO_3^-_{(aq)}$ and $HNO_3_{(g)} \leftrightarrow HNO_3_{(aq)}$, respectively: $K_{1b} = K_1 / K_{1a}$.

◊ The equilibrium constant $K_{2b}$ of the reaction $HCl_{(aq)} \leftrightarrow H^+_{(aq)} + Cl^-_{(aq)}$ is calculated from $K_2$ and $K_{2a}$ of the reactions $HCl_{(g)} \leftrightarrow H^+_{(aq)} + Cl^-_{(aq)}$ and $HCl_{(g)} \leftrightarrow HCl_{(aq)}$, respectively: $K_{2b} = K_2 / K_{2a}$. 

− Data not available.
Table 3. Potential species for the five aerosol types\(^1\).

| \(R_1\) | \(R_2\) | \(R_3\) | Aerosol Type                 | Major Species                                                                 | Minor Species                                                                 |
|--------|--------|--------|-----------------------------|------------------------------------------------------------------------------|------------------------------------------------------------------------------|
| \(R_1 < 1\) | any value | any value | Sulfate Rich (free acid)  | NaHSO\(_4\), NH\(_4\)HSO\(_4\), KHSO\(_4\), CaSO\(_4\) | Na\(^+\), NH\(_4\)\(^+\), H\(^+\), HSO\(_4\)\(^-\), SO\(_4\)\(^2-\), NO\(_3\)\(^-\), Cl\(^-\), Ca\(^{2+}\), K\(^+\), H\(_2\)O | NH\(_3\)(aq), NO\(_3\)(aq), Cl\(_{(aq)}\), NH\(_3\)(aq), HNO\(_3\)(aq), HCl\(_{(aq)}\), HSO\(_4\) |
| \(1 \leq R_1 < 2\) | any value | any value | Sulfate Rich               | NaHSO\(_4\), NH\(_4\)HSO\(_4\), Na\(_2\)SO\(_4\), (NH\(_4\)\(_2\))SO\(_4\), CaSO\(_4\), K\(_2\)SO\(_4\), MgSO\(_4\) | Na\(^+\), NH\(_4\)\(^+\), H\(^+\), HSO\(_4\)\(^-\), SO\(_4\)\(^2-\), NO\(_3\)\(^-\), Cl\(^-\), Ca\(^{2+}\), K\(^+\), Mg\(^{2+}\), H\(_2\)O | NH\(_3\)(aq), NO\(_3\)(aq), Cl\(_{(aq)}\), NH\(_3\)(aq), HNO\(_3\)(aq), HCl\(_{(aq)}\) |
| \(R_1 \geq 2\) | \(R_2 < 2\) | any value | Sulfate Poor, Crustals & Sodium Poor | Na\(_2\)SO\(_4\), (NH\(_4\)\(_2\))SO\(_4\), NH\(_4\)NO\(_3\), NH\(_4\)Cl, CaSO\(_4\), K\(_2\)SO\(_4\), MgSO\(_4\) | Na\(^+\), NH\(_4\)\(^+\), H\(^+\), SO\(_4\)\(^2-\), NO\(_3\)\(^-\), Cl\(^-\), Ca\(^{2+}\), Mg\(^{2+}\), H\(_2\)O, NH\(_3\)(aq), HNO\(_3\)(aq), HCl\(_{(aq)}\) | HSO\(_4\) |
| \(R_1 \geq 2\) | \(R_2 \geq 2\) | \(R_3 < 2\) | Sulfate Poor, Crustals & Sodium Rich, Crustals Poor | NaNO\(_3\), NaCl, NH\(_4\)NO\(_3\), NH\(_4\)Cl, CaSO\(_4\), K\(_2\)SO\(_4\), MgSO\(_4\) | Na\(^+\), NH\(_4\)\(^+\), H\(^+\), SO\(_4\)\(^2-\), NO\(_3\)\(^-\), Cl\(^-\), Ca\(^{2+}\), K\(^+\), Mg\(^{2+}\), H\(_2\)O, NH\(_3\)(aq), HNO\(_3\)(aq), HCl\(_{(aq)}\) | HSO\(_4\) |
| \(R_1 \geq 2\) | \(R_2 \geq 2\) | \(R_3 > 2\) | Sulfate Poor, Crustals & Sodium Rich, Crustals Rich | NaNO\(_3\), NaCl, NH\(_4\)NO\(_3\), NH\(_4\)Cl, CaSO\(_4\), K\(_2\)SO\(_4\), MgSO\(_4\), Ca(NO\(_3\))\(_2\), CaCl\(_2\), Mg(NO\(_3\))\(_2\), MgCl\(_2\), KNO\(_3\), KCl | Na\(^+\), NH\(_4\)\(^+\), H\(^+\), SO\(_4\)\(^2-\), NO\(_3\)\(^-\), Cl\(^-\), Ca\(^{2+}\), Mg\(^{2+}\), H\(_2\)O, NH\(_3\)(aq), HNO\(_3\)(aq), HCl\(_{(aq)}\) | HSO\(_4\) |

\(^1\) Species in bold are new in ISORROPIA II.
Table 4. Deliquescence relative humidities, temperature dependence and parameter $q$ values for all the salts modeled in ISORROPIA II$^2$.

| Salt              | DRH (298.15 K) | $\frac{18}{1000R}L_s m_s$ | $q$  |
|-------------------|----------------|---------------------------|------|
| Ca(NO$_3$)$_2$    | 0.4906         | -430.5                    | 0.93 |
| CaCl$_2$          | 0.2830         | -1121.0                   | 2.40 |
| CaSO$_4$          | 0.9700         | -                          | -    |
| KHSO$_4$          | 0.8600         | -                          | -    |
| K$_2$SO$_4$       | 0.9751         | 35.6                       | -0.25|
| KNO$_3$           | 0.9248         | -                          | -2.33|
| KCl$^-$           | 0.8426         | 158.9                      | 0.92 |
| MgSO$_4$          | 0.8613         | -714.5$^*$                 | 0.15 $^*$|
| Mg(NO$_3$)$_2$    | 0.5400         | -                          | 2.32 |
| MgCl$_2$          | 0.3284         | -1860.2                    | 2.90 |
| NaCl$^*$          | 0.7528         | 25.0                       | 2.23 |
| Na$_2$SO$_4$      | 0.9300         | 80.0                       | -0.19|
| NaNO$_3$          | 0.7379         | 304.0                      | -0.39|
| (NH$_4$)$_2$SO$_4$| 0.7997         | 80.0                       | -0.25|
| NH$_4$NO$_3$      | 0.6183         | 852.0                      | -1.15|
| NH$_4$Cl$^+$      | 0.7710         | 239.0                      | 0.82 |
| NH$_4$HSO$_4$     | 0.4000         | 384.0 (+),$^c$             |      |
| NaHSO$_4$         | 0.5200         | -45.0 (+),$^d$             |      |
| (NH$_4$)$_3$H(SO$_4$)$_2$ | 0.6900     | 186.0 (+),$^e$             |      |
| H$_2$SO$_4$       | 0.000          | -                          | 0.70 |
| H-HSO$_4$         | 0.000          | -                          | 8.00 |
| HNO$_3$           | N/A            | -                          | 2.60 |
| HCl$^+$           | N/A            | -                          | 6.00 |

$^*$ Kim and Seinfeld (1995); $^{\checkmark}$ Pilinis and Seinfeld (1989); $^\diamond$ Ha and Chan (1999); $^\triangle$ Kim et al. (1993); $^-$ Data not available. $^a\gamma_{CaSO_4} = 0$; $^b\gamma_{KHSO_4} = \frac{\gamma_{H-\text{HSO}_4} \gamma_{KCl}}{\gamma_{HCl}}$; $^{c}\gamma_{NH_4\text{HSO}_4} = \frac{\gamma_{H-\text{HSO}_4} \gamma_{NH_4\text{Cl}}}{\gamma_{HCl}}$; $^{d}\gamma_{Na\text{HSO}_4} = \frac{\gamma_{H-\text{HSO}_4} \gamma_{NaCl}}{\gamma_{HCl}}$; $^{e}\gamma_{(NH_4)_3\text{H(SO}_4)_2} = \left(\gamma_{(NH_4)_2\text{SO}_4}^3 \cdot \gamma_{NH_4\text{HSO}_4}\right)^{0.2}$

$^2$ Species in bold are new in ISORROPIA II.
Table 5. Mutual deliquescence relative humidities, for the new salts modeled in ISORROPIA II³.

| Salt Mixture                                                                 | MDRH³  |
|------------------------------------------------------------------------------|--------|
| Ca(NO₃)₂, CaCl₂, K₂SO₄, KNO₃, KCl, MgSO₄, Mg(NO₃)₂, MgCl₂, NaNO₃, NaCl, NH₄NO₃, NH₄Cl | 0.200  |
| (NH₄)₂SO₄, NH₄NO₃, NH₄Cl, Na₂SO₄, K₂SO₄, MgSO₄                               | 0.460  |
| Ca(NO₃)₂, K₂SO₄, KNO₃, KCl, MgSO₄, Mg(NO₃)₂, MgCl₂, NaNO₃, NaCl, NH₄NO₃, NH₄Cl | 0.240  |
| (NH₄)₂SO₄, NH₄Cl, Na₂SO₄, K₂SO₄, MgSO₄                                      | 0.691  |
| Ca(NO₃)₂, K₂SO₄, KNO₃, KCl, MgSO₄, Mg(NO₃)₂, NaNO₃, NaCl, NH₄NO₃, NH₄Cl      | 0.240  |
| (NH₄)₂SO₄, Na₂SO₄, K₂SO₄, MgSO₄                                             | 0.697  |
| K₂SO₄, MgSO₄, KHSO₄, NH₄HSO₄, NaHSO₄, (NH₄)₂SO₄, Na₂SO₄, (NH₄)₃H(SO₄)₂      | 0.240  |
| (NH₄)₂SO₄, NH₄NO₃, Na₂SO₄, K₂SO₄, MgSO₄                                      | 0.494  |
| K₂SO₄, KNO₃, KCl, MgSO₄, Mg(NO₃)₂, NaNO₃, NaCl, NH₄NO₃, NH₄Cl                | 0.240  |
| K₂SO₄, MgSO₄, KHSO₄, NaHSO₄, (NH₄)₂SO₄, Na₂SO₄, (NH₄)₃H(SO₄)₂               | 0.363  |
| K₂SO₄, KNO₃, KCl, MgSO₄, NaNO₃, NaCl, NH₄NO₃, NH₄Cl                          | 0.596  |
| K₂SO₄, MgSO₄, KHSO₄, (NH₄)₂SO₄, Na₂SO₄, (NH₄)₃H(SO₄)₂                      | 0.610  |
| Ca(NO₃)₂, K₂SO₄, KNO₃, KCl, MgSO₄, Mg(NO₃)₂, NaNO₃, NaCl, NH₄NO₃, NH₄Cl      | 0.240  |
| K₂SO₄, KNO₃, KCl, MgSO₄, Mg(NO₃)₂, NaNO₃, NaCl, NH₄NO₃, NH₄Cl                | 0.240  |

* Obtained from Potukuchi and Wexler (1995a, b) for mixtures with closest composition (T=298.15 K).

³ Species in italics determine the mixture from which the MDRH value has been taken for each case.
Table 6. Coefficients of \( m(a_w) \) from the polynomial fit \( m(a_w) = k_0 + k_1 a_w + k_2 a_w^2 + \ldots \).

| Species          | \( k_0 \)   | \( k_1 \)   | \( k_2 \)   | \( k_3 \)   | \( k_4 \)   | \( k_5 \)   |
|------------------|-------------|-------------|-------------|-------------|-------------|-------------|
| Ca(NO\(_3\))\(_2\)^\* | 34.400     | -155.360   | 438.210     | -706.380    | 579.230     | -190.270    |
| CaCl\(_2\)       | 20.847     | -97.599    | 273.220     | -422.120    | 331.160     | -105.450    |
| CaSO\(_4\)       | N/A        | N/A        | N/A         | N/A         | N/A         | N/A         |
| KHSO\(_4\)^§     | 1.061      | -0.101     | 1.579x10\(^{-2}\) | -1.950x10\(^{-3}\) | 9.515x10\(^{-5}\) | -1.547x10\(^{-6}\) |
| K\(_2\)SO\(_4\)^♣ | 1061.51    | -4748.97   | 8096.16     | -6166.16    | 1757.47     | 0           |
| KNO\(_3\)^♦      | 1.2141x10\(^4\) | -5.1173x10\(^{-4}\) | 8.12524x10\(^4\) | -5.7527x10\(^{-4}\) | 1.5305x10\(^4\) | 0           |
| KCl               | 179.721    | -721.266   | 1161.03     | -841.479    | 221.943     | 0           |
| MgSO\(_4\)^♦     | -0.778     | 177.740    | -719.790    | 1174.600    | -863.440    | 232.310     |
| Mg(NO\(_3\))\(_2\)^♦ | 12.166     | -16.154    | 0           | 10.886      | 0           | -6.815      |
| MgCl\(_2\)^♦     | 11.505     | -26.518    | 34.937      | -19.829     | 0           | 0           |

\(^\*\) The coefficients for Ca(NO\(_3\))\(_2\) given by Kim and Seinfeld (1995) contain a typographical error. The coefficients used here were obtained by fitting the equation \( m(a_w) = k_0 + k_1 a_w + k_2 a_w^2 + k_3 a_w^3 + k_4 a_w^4 + k_5 a_w^5 \) to their Fig. 15.

\(*\) source: Kim and Seinfeld (1995).

\(^\dagger\) source: Kelly and Wexler (1995).

\(^\§\) Same as NaHSO\(_4\).

\(^\diamond\) source: Ha and Chan (1999).
Table 7. List of input conditions for model simulations\textsuperscript{a}.

| Case | Aerosol Type | Na    | H\textsubscript{2}SO\textsubscript{4} | NH\textsubscript{3} | HNO\textsubscript{3} | HCl    | Ca\textsuperscript{2+} | K\textsuperscript{+} | Mg\textsuperscript{2+} | R\textsubscript{1}, R\textsubscript{2}, R\textsubscript{3} |
|------|--------------|-------|----------------|----------------|----------------|--------|----------------|----------------|----------------|------------------|
| 1    | Urban (1)    | 0.000 | 10.000          | 3.400           | 2.000          | 0.000  | 0.400          | 0.330          | 0.000          | 2.14, 0.18, 0.18 |
| 2    | Urban (2)    | 0.023 | 10.000          | 3.400           | 2.000          | 0.037  | 0.900          | 1.000          | 0.000          | 2.44, 0.48, 0.47 |
| 3    | Urban (3)    | 0.000 | 15.000          | 2.000           | 10.000         | 0.000  | 0.900          | 1.000          | 0.000          | 1.27, 0.31, 0.32 |
| 4    | Urban (4)    | 0.000 | 15.000          | 2.000           | 10.000         | 0.400  | 0.330          | 0.330          | 0.000          | 0.89, 0.12, 0.12 |
| 5    | N-u Cont.\textsuperscript{b} (1) | 0.200 | 2.000           | 8.000           | 12.000         | 0.200  | 0.120          | 0.180          | 0.180          | 0.000, 0.000, 0.000 |
| 6    | N-u Cont. (2) | 0.100 | 4.000           | 10.000          | 7.000          | 0.100  | 0.120          | 0.180          | 0.180          | 0.050, 0.050, 0.050 |
| 7    | N-u Cont. (3) | 0.023 | 5.664           | 12.000          | 2.000          | 0.037  | 0.120          | 0.180          | 0.180          | 0.050, 0.050, 0.050 |
| 8    | N-u Cont. (4) | 0.023 | 5.664           | 20.400          | 0.611          | 0.037  | 0.120          | 0.180          | 0.180          | 0.050, 0.050, 0.050 |
| 9    | Marine (1)   | 2.000 | 1.000           | 0.010           | 0.300          | 3.121  | 0.100          | 0.100          | 0.070          | 9.36, 9.30, 0.80 |
| 10   | Marine (2)   | 1.500 | 1.000           | 0.010           | 1.500          | 2.500  | 0.360          | 0.450          | 0.050          | 8.66, 8.60, 2.21 |
| 11   | Marine (3)   | 2.500 | 3.000           | 0.001           | 3.000          | 2.500  | 0.500          | 1.000          | 0.050          | 4.86, 4.86, 1.31 |
| 12   | Marine (4)   | 3.000 | 3.000           | 0.020           | 2.000          | 3.121  | 0.360          | 0.450          | 0.130          | 5.14, 5.10, 0.84 |
| 13   | Rem. Cont.\textsuperscript{b} (1) | 0.000 | 10.000          | 4.250           | 0.145          | 0.000  | 0.080          | 0.090          | 0.000          | 2.49, 0.04, 0.04 |
| 14   | Rem. Cont. (2) | 0.023 | 10.000          | 3.000           | 1.000          | 0.037  | 0.080          | 0.090          | 0.000          | 1.78, 0.05, 0.04 |
| 15   | Rem. Cont. (3) | 0.100 | 15.000          | 3.000           | 4.000          | 0.100  | 0.080          | 0.090          | 0.000          | 1.21, 0.06, 0.03 |
| 16   | Rem. Cont. (4) | 0.200 | 15.000          | 3.000           | 8.000          | 0.200  | 0.080          | 0.090          | 0.040          | 1.25, 0.10, 0.04 |

\textsuperscript{a} Simulations for each case were conducted for 10, 25, 40, 55, 65, 70, 75, 80, 85, 90 and 98\% relative humidity. Temperature was set to 298.15 K. Concentration given in \( \mu g m^{-3} \). \textsuperscript{b} N-u Cont., non-urban continental; Rem. Cont., remote continental.
Table 8. Normalized mean errors between ISORROPIA II and SCAPE2 for the simulations in Table 7.

| NME (%)         | $H_2O_{(p)}$ | $NO_3_{(p)}$ | $Cl_{(p)}$ | $NH_4_{(p)}$ | Total PM | $H^+_{(aq)}$ |
|-----------------|--------------|--------------|------------|--------------|----------|-------------|
| ISORROPIA-II (Stable) | 13.5         | 16.5         | 6.5        | 2.1          | 13.0     | 64.9        |
| ISORROPIA-II (Metastable) | 14.7         | 23.7         | 6.6        | 6.7          | 14.3     | 68.0        |
### Table 9. CPU time required for the simulations in Table 7.

| Aerosol Case          | Convergence criterion | ISORROPIA II (stable) CPU time (msec) | SCAPE2 CPU time (msec) | CPU<sub>SCAPE2</sub> | CPU<sub>ISORROPIA-II</sub> | CPU<sub>ISORROPIA-II</sub>(stable) | CPU<sub>ISORROPIA-II</sub>(metastable) | CPU<sub>ISORROPIA-II</sub> |
|-----------------------|-----------------------|---------------------------------------|------------------------|-----------------------|-----------------------------|--------------------------------------|-------------------------------------|-----------------------------|
| Marine                | 30                    | 50                                    | 16.7                   | 1.16                  | 1.0                         |                                     |                                     | 1.0                         |
| Urban                 | 20                    | 210                                   | 10.5                   | 1.09                  | 1.0                         |                                     |                                     | 1.0                         |
| Remote continental    | 20                    | 440                                   | 22.0                   | 1.05                  | 1.0                         |                                     |                                     | 1.0                         |
| Non-urban continental | 20                    | 110                                   | 5.5                    | 1.00                  | 1.0                         |                                     |                                     | 1.0                         |
| Marine                | 10⁻³                  | 30                                    | >1000                  | 1.16                  | 1.0                         |                                     |                                     | 1.0                         |
| Urban                 | 10⁻³                  | 20                                    | 14.0                   | 1.09                  | 1.0                         |                                     |                                     | 1.0                         |
| Non-urban continental | 10⁻³                  | 20                                    | >1000                  | 1.05                  | 1.0                         |                                     |                                     | 1.0                         |
| Marine                | 10⁻⁴                  | 20                                    | >1000                  | 1.00                  | 1.0                         |                                     |                                     | 1.0                         |
| Urban                 | 10⁻⁴                  | 20                                    | >1000                  | 1.06                  | 1.0                         |                                     |                                     | 1.0                         |
| Non-urban continental | 10⁻⁴                  | 20                                    | >1000                  | 1.00                  | 1.0                         |                                     |                                     | 1.0                         |
| Marine                | 10⁻⁵                  | 20                                    | >1000                  | 1.05                  | 1.0                         |                                     |                                     | 1.0                         |
| Urban                 | 10⁻⁵                  | 20                                    | >1000                  | 1.00                  | 1.0                         |                                     |                                     | 1.0                         |
| Non-urban continental | 10⁻⁵                  | 20                                    | 1250                   | 1.00                  | 1.0                         |                                     |                                     | 1.0                         |
**Input:** RH, T, Concentrations of NH$_3$, H$_2$SO$_4$, Na, HCl, HNO$_3$, Ca, K, Mg

Calculate $R_1$, $R_2$, $R_3$

Determine possible major species (Table 3) and RH subdomain

Calculate Equilibrium Reaction Constants (Tables 1,2) for "Forward" or "Reverse" problem

Stable Solution? Metastable Solution?

Solid + Liquid Aerosol Liquid Aerosol (no solids present)

mass conservation, activity coefficient and electroneutrality computations

Major Species concentration

Calculate Minor Species concentration

**Output:** Equilibrium Concentration of species in Gas, Solid and Liquid phase

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**Fig. 1.** Generic solution procedure of ISORROPIA II.
Fig. 2. DRH as a function of temperature for all ISORROPIA salts.
Fig. 3. Concentration of aerosol water (a), nitrate (b), chloride (c), ammonium (d), total PM (e), and hydrogen (f), as predicted by ISORROPIA II (thermodynamically stable solution) and SCAPE2 for all the conditions described in Table 7. Temperature is set to 298.15 K.
Fig. 4. Same as Fig. 2 but using the metastable solution of ISORROPIA II.
Fig. 5. Concentration of aerosol water (a), aqueous potassium (b), aqueous ammonium (c), and aqueous nitrate (d) as predicted by ISORROPIA II (thermodynamically stable solution) and SCAPE2 for the urban (3) case (Table 7) corresponding to a sulfate rich aerosol behavior ($1 < R_1 < 2$). Temperature is set to 298.15 K.
Fig. 6. Concentration of aerosol water (a), aqueous potassium (b), solid sodium chloride (c), and aqueous magnesium (d) as predicted by ISORROPIA II (thermodynamically stable solution) and SCAPE2 for the marine (4) case (Table 7) corresponding to a sulfate poor, crustals and sodium rich aerosol behavior ($R_1 > 2, R_2 > 2$). Temperature is set to 298.15 K.
Fig. 7. Concentration of aerosol water (a), aqueous nitrate (b), and aqueous ammonium (c) as a function of relative humidity as predicted by ISORROPIA II (thermodynamically stable solution) and SCAPE2 for the non-urban continental (1) case (Table 7) corresponding to a sulfate poor, ammonium rich aerosol behavior ($R_1>2$, $R_2<2$). Temperature is set to 298.15 K.
**Fig. 8.** Concentration of aerosol water (a), and aqueous phase potassium (b) as a function of relative humidity as predicted by ISORROPIA II (using the thermodynamically stable and metastable solutions) and SCAPE2 for the remote continental (1) case (Table 7) corresponding to a sulfate near-neutral aerosol behavior. Temperature is set to 298.15 K.