MODELING ATMOSPHERIC AEROSOLS USING THERMODYNAMIC ARGUMENTS - A REVIEW

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ABSTRACT

Atmospheric aerosols have been implicated in human health effects, visibility reduction in urban and regional areas, acidic deposition, and altering the earth's radiation balance. A major goal of scientific research for the last fifteen years has been the development of the necessary models, using first principles, that can be used in order to predict the size and composition of atmospheric particulate matter. A number of such models assume that atmospheric aerosols are at thermodynamic equilibrium with the corresponding gases, and they predict the chemical composition of atmospheric aerosols, using thermodynamic arguments. The current state of the art of thermodynamic equilibrium models is reviewed in this paper, and the theory used is presented.

INTRODUCTION

Atmospheric aerosols are airborne particles that are composed of water, inorganic salts, insoluble materials (dust, crustal material) organics (soot, VOC) and trace metals. The size of these particles cover a broad range, and the composition and mechanisms that generate them differ for each size section.

Knowledge of the physical state and composition of these particles is of great importance because of the role they play in important atmospheric processes. The major effect of aerosol is in the earth's climate (climate forcing), which is achieved by altering the radiation balance both through direct and indirect mechanisms. Direct forcing is the effect in-duced by scattering and absorption of solar radiation from the particles themselves. Indirect forcing is the effect of aerosols on cloud optical depth and albedo, caused by alteration of the available cloud condensation nuclei (CCN). Changes of CCN concentration affect the droplet size distribution, size and coverage of clouds on both a temporal and a spatial scale. Specifically, an increase of CCN leads to smaller droplet sizes, yielding brighter and more reflective clouds. Estimating indirect forcing is of great importance, because of its significance in the planetary radiation budget. For example, marine boundary layer clouds contribute to about one third of the

Earth's albedo (Charlson et al., 1987). Because of the nonuniform geographical distribution of aerosols and the complex mechanisms which they are involved in, it is well recognized that aerosol production is the most uncertain and elusive of all anthropogenic activities affecting climate.

Marine aerosols also play an important role in the DMS sulfur cycle, by providing a medium for heterogeneous conversion of SO_2 to non-sea salt sulfate (nss). This pathway affects the available CCN (Russell et al., 1994), and is one of the mechanisms involved in indirect climate forcing of aerosols. Because of their interaction with electromagnetic radiation, aerosols also impair visibility. Due to their chemical composition, especially when mixed with polluted air rich in SO_2 and NO_x from continental sources, these aerosols can produce acid rain, which causes structural erosion and degradation of soil and water quality. There has also been a concern about the effect of acidic aerosol on public health (Saxena et al., 1986).

Inorganic salts comprise 25-50% of dry total fine aerosol mass (Heintzenberg, 1989) and together with water consist a significant portion of the total aerosol mass (especially in high relative humidity environments). The inorganic salts found are mainly those of ammonium, sodium, sulfate, nitrate and chloride. Total particle concentrations are fairly uniform throughout the tropical regions, and range between 100 to 300 cm^{-3} (Fitzgerald, 1991). The aerosol size distribution is characterized by 3 modes; the nuclei region ($D_p < 0.1\mu m$), accumulation mode ($0.1\mu m < D_p < 0.5\mu m$), and the coarse mode ($D_p > 0.5\mu m$) (Pandis et al., 1995). Nuclei are generated by the homogeneous heteromolecular nucleation of H_2SO_4 vapor produced from the gas phase oxidation of SO_2 and methanosulfonic acids by OH radicals. Although the mechanism for developing the accumulation mode is still unclear, the prevailing hypothesis is that this section is the result of cloud formation and evaporation cycles (Pandis et al., 1995). Cloud formation allows the heterogeneous oxidation of SO_2 to form sulfate in the droplets, reacting with sea salt that might exist in the cloud droplets. As a result, this increases the dry aerosol mass and changes the composition of cloud droplets. Coarse particles are mainly composed of sea salt, and are generated from the evaporation of sea water droplets produced from bubble bursting and wind-induced

wave breaking. Coarse mode particles also contain small amounts of nitrate and mineral dust (normally up to 5% of sea salt mass) although occasionally, dust concentrations can reach very high levels, comparable to that of sea salt (Fitzgerald, 1991).

In order to calculate the mass and composition of aerosols, a common assumption made is that volatile species in the gas and aerosol phases are in chemical equilibrium. Although in many cases this has proven to be a valid assumption, there are situations in which the time needed to achieve chemical equilibrium is long compared to the time in which local air and particles remain in contact. When this happens, the equilibrium approach is not valid and a model incorporating transfer processes should be applied (Wexler and Seinfeld, 1991). However, the cases in which such an approach is needed are limited to coarse particle sizes and cool (Meng and Seinfeld, 1996). Experimental evidence for the nonequilibrium state has been found (Allen et al., 1989), but for marine aerosols and/or warmer environments, the thermodynamic equilibrium assumption is valid and has been experimentally confirmed (Hildemann et al., 1984; Quinn et al., 1992).

In this paper the current state of the ability to model atmospheric aerosol behavior from first thermodynamic principles is reviewed and the best thermodynamic models available in the scientific community are presented. The equations and the methodologies used, as well as their advantages and disadvantages are described.

EQUILIBRIUM MODELING FORMULATION

The essential element of an equilibrium model is a complete phase and chemical equilibrium calculation for the system considered. The condition for chemical equilibrium in a closed system at constant temperature T and pressure p is that the total Gibbs free energy of the system G is minimum. The Gibbs free energy is a function of T, p and the concentrations of the components in the system, n_i. Thus determination of the equilibrium composition of the system is a minimization problem:

$$\min G(T, p, n_i) \qquad (1)$$

subject to T, p constant, $n_i > 0$ and conservation of mass. The condition for a minimum G is equivalent to (Denbigh, 1981):

$$\sum_i \nu_{ij}\mu_i = 0 \quad \text{for all reactions } j \qquad (2)$$

where, ν_{ij} is the stoichiometric coefficient of the i-th species in the j-th reaction and $\mu_i = \left(\dfrac{\partial G}{\partial n_i}\right)_{T,p,n_j}$ is the chemical potential of species i. To solve the system (2), expressions for the chemical potentials are needed.

The chemical potential of a species i is given by the expression:

$$\mu_i = \mu_i^o(T) + RT \ln a_i \qquad (3)$$

where, $\mu_i^o(T)$ is the standard chemical potential for 1 atm and temperature T (in K), R is the universal gas constant and a_i the activity of the i-th species. For solids, $a_i = 1$. For ideal gases $a_i = p_i$, where p_i is the partial pressure of the i-th species. For aqueous solutions of electrolytes, $a_i = \gamma_i^{(\nu_+ + \nu_-)} m_+^{\nu_+} m_-^{\nu_-}$,
where, γ_i is the activity coefficient of species i in water, n_+ and n_- are the moles of cations and anions, respectively, released per mole of electrolyte and m_+, m_- are their molalities, respectively. For electrolytes, the standard chemical potential is related to the standard chemical potentials of the cations and anions, $\mu_{i_+}^o(T)$, $\mu_{i_-}^o(T)$ with the relationship:

$$\mu_i^o(T) = \nu_+ \mu_{i_+}^o(T) + \nu_- \mu_{i_-}^o(T) \qquad (4)$$

After substituting (3) into (2) and rearranging:

$$\prod_i a_i^{\nu_{ij}} = K_j(T) \qquad (5)$$

where $K_j(T)$ is the equilibrium constant of the j-th reaction,

$$K_j(T) = \exp\left[-\frac{\sum_i \nu_{ij}\mu_i^o(T)}{RT}\right] \qquad (6)$$

The system of Equations (5) is the one that determines the equilibrium concentration of all species i.

To determine the equilibrium constant at a temperature T, the Van't Hoff equation is used:

$$\frac{d\ln K(T)}{dT} = \frac{\Delta H^o(T)}{RT^2} \qquad (7)$$

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

$$\Delta H^o(T) = \Delta H^o(T_o) + \Delta c_p^o(T - T_o) \qquad (8)$$

where $\Delta H^o(T_0)$ is the standard enthalpy change at a reference temperature (usually 298.15 K) and Δc_p^0 is the change of heat capacity at T_0.

A simplification is possible in the expression for the chemical potential of water vapor. Since water is by far the most plentiful gaseous species of those involved in equilibrium, the change in the vapor pressure of water from that in the ambient air is negligible. Thus, the relative humidity can be treated as constant and known for the calculation. Phase equilibrium between gas and aerosols gives that the water activity, a_w, is equal to the ambient relative humidity (Bassett and Seinfeld, 1983):

$$a_w = RH \qquad (9)$$

where RH is expressed on a fractional (0-1) scale.

The water activity a_w is calculated using empirical mixing rules. Among the different expressions used to estimate the water activity in a high ionic strength solution, like the ones in atmospheric aerosols, the mixing rules of ZSR (Pilinis and Seinfeld, 1987) and Kusik and Meissner (1978) have been shown to adequately correlate experimental data.

The ZSR correlation can be expressed as:

$$\sum_i \frac{m_i}{m_{oi}(a_w)} = 1 \qquad (10)$$

where m_i is the molality of the i-th electrolyte in the multicomponent solution and $m_{oi}(a_w)$ is the molality of an aqueous solution of species i with the same water activity as the multicomponent solution. Equation (10) is rewritten in a way to explicitly calculate aerosol water content. By definition, molality is $m_i = \dfrac{M_i}{W}$, where M_i is the molar concentration of species i in the air (mol m^{-3} air) and W is the mass concentration of aerosol water in the air (kg m^{-3} air). Hence, by substituting m_i into Equation (10), the water content of the aerosols, W is calculated by:

$$W = \sum_i \frac{M_i}{m_{oi}(a_w)} \qquad (11)$$

The Kusik and Meissner rule can be expressed as:

$$\ln a_w = \sum_{ij} \frac{m_{ij}}{2I} \frac{n_{ij}z_iz_j}{z_i+z_j} \left[\sum_{even\ k} \left(\frac{z_i+z_k}{2} \right)^2 z_k \frac{m_k}{I} \ln a_{wik}^o + \right.$$

$$\left. + \sum_{odd\ k} \left(\frac{z_j+z_k}{2} \right)^2 z_k \frac{m_k}{I} \ln a_{wjk}^o \right] +$$

$$+ \frac{M_w}{10^3} \sum_{ij} \frac{n_{ij}m_{ij}}{z_i+z_j} \left[z_i \left(\sum_{even\ k} \left(\frac{z_i+z_k}{2} \right)^2 \frac{m_k}{I} - 1 \right) + \right.$$

$$\left. + z_j \left(\sum_{odd\ k} \left(\frac{z_j+z_k}{2} \right)^2 \frac{m_k}{I} - 1 \right) \right] \quad (12)$$

where, a_{wij}^o is the water activity for a solution containing only ions ij, m_{ij} is the molality of electrolyte ij, n_{ij} is the number of moles of ions into which each mole of ij dissociates and m_k is the molality of ion k.

Most of the methods that predict the activity coefficients of a multicomponent solution are empirical, or semi-empirical and typically use the activity coefficients of single-electrolyte solutions of the same ionic strength. The main rules used to calculate multicomponent activity coefficients are those developed by Bromley (1973), Kusik and Meissner (1978) and Pitzer and Mayorga (1973).

The Bromley formula for multicomponent activity coefficients is:

$$\log \gamma_{12} = -A_\gamma \frac{z_1z_2I^{1/2}}{1+I^{1/2}} + \frac{z_1z_2}{z_1+z_2} \left[\frac{F_1}{z_1} + \frac{F_2}{z_2} \right] \quad (13)$$

where, γ_{12} is the activity coefficient of Cation 1 and Anion 2, A_γ is the Debye-Huckel constant, which has a value of 0.511 kg$^{0.5}$ mol$^{-0.5}$ at 298.15 K, and,

$$F_1 = Y_{21} \log \gamma_{12}^o + Y_{41} \log \gamma_{14}^o + Y_{61} \log \gamma_{16}^o + \ldots$$

$$+ \frac{A_\gamma I^{1/2}}{1+I^{1/2}} \left[z_1z_2Y_{21} + z_1z_4Y_{41} + z_1z_6Y_{61} + \ldots \right] \quad (14)$$

$$F_2 = X_{12} \log \gamma_{12}^o + X_{32} \log \gamma_{32}^o + X_{52} \log \gamma_{52}^o + \ldots$$

$$+ \frac{A_\gamma I^{1/2}}{1+I^{1/2}} \left[z_1z_2X_{12} + z_3z_2X_{32} + z_5z_2X_{52} + \ldots \right] \quad (15)$$

$$Y_{21} = \left(\frac{z_1+z_2}{2} \right)^2 \frac{m_2}{I} \quad (16)$$

$$X_{12} = \left(\frac{z_1+z_2}{2} \right)^2 \frac{m_1}{I} \quad (17)$$

I is the ionic strength of the solution,

$$I = \frac{1}{2} \sum_i m_i z_i^2 \quad (18)$$

z_i is the absolute charge of ionic species i, and γ_{ij}^o is the mean ionic activity coefficient of the binary pair i-j (binary activity coefficient) for a solution that contains only i-j ions at the ionic strength of the multicomponent solution. In Equations (13) to (17), odd subscripts refer to cations, while even subscripts refer to anions.

The Kusik and Meissner formula for multicomponent activity coefficients is:

$$\log \gamma_{12}(\text{K}-\text{M}) = \log \gamma_{12}(\text{Bromley}) + \frac{A_\gamma z_1z_2I^{1/2}}{1+I^{1/2}}$$

$$\cdot \left[1 - \frac{1}{z_1+z_2 I} \left(\begin{array}{c} z_2m_2 \left(\frac{z_1+z_2}{2} \right)^2 + z_4m_4 \left(\frac{z_1+z_4}{2} \right)^2 + \\ + \cdots + z_1m_1 \left(\frac{z_1+z_2}{2} \right)^2 + z_3m_3 \left(\frac{z_3+z_2}{2} \right)^2 + \cdots \end{array} \right) \right]$$

(19)

Thus, the Kusik and Meissner formula can be viewed as a correction to the Bromley method. It has to be noted that, if all the ion species are singly charged, both methods reduce to the same expression (Kim et al., 1993).

The Pitzer method (Pitzer and Kim, 1974) is derived from the definition of the excess Gibbs free energy. After taking the derivative of the equation for the excess Gibbs free energy and combining coefficients into measureable parameters, one gets (Kim et al., 1993):

$$\ln \gamma_{12} = \frac{(\nu_1 \ln \gamma_1 + \nu_2 \ln \gamma_2)}{\nu_1 + \nu_2} \quad (20)$$

where, γ_1 and γ_2 are the activity coefficients of the cation and the anion of interest, and ν_1, ν_2 are the numbers of ions 1 and 2 in the neutral salt, respectively. Pitzer's method has been used to calculate the solubility of several minerals in concentrated solutions, but, as pointed out by Clegg and Brimblecombe (1988), its reliability beyond this range of molality has not been verified.

As shown in Equations 13 and 19, both Kusik and Meissner and Bromley's methods need the binary

activity coefficients of the corresponding salts. Two formulas have been used to calculate the binary activity coefficients, the method of Kusik and Meissner and Pitzer's method. The Kusik and Meissner formula for binary activity coefficients is (Kusik and Meissner, 1978):

$$\log \gamma_{12}^o = z_1 z_2 \log \Gamma^o \quad (21)$$

where,

$$\Gamma^o = \left[1 + B(1+0.1I)^q - B\right]\Gamma^* \quad (22)$$

$$B = 0.75 - 0.065q \quad (23)$$

$$\log \Gamma^* = \frac{-0.5107 I^{1/2}}{1 + C I^{1/2}} \quad (24)$$

$$C = 1 + 0.055q \exp\left(-0.023 I^3\right) \quad (25)$$

q is a parameter specific for each salt.

The Pitzer formula for binary activity coefficients is (Pilinis and Seinfeld, 1987; Pitzer and Mayorga, 1973):

$$\ln \gamma_{12}^o = z_1 z_2 f^\gamma$$
$$+ m_{12} \frac{2\nu_1\nu_2}{\nu_1 + \nu_2} B_{12}^\gamma + m_{12}^2 \frac{2(\nu_1\nu_2)^{3/2}}{\nu_1 + \nu_2} C_{12}^\gamma \quad (26)$$

where, ν_1, ν_2 are the numbers of ions 1 and 2 in the neutral salt, m_{12} is the molality of the electrolyte in the binary solution for the given ionic strength, and where

$$f^\gamma = -0.392\left[\frac{I^{1/2}}{1+1.2I^{1/2}} + \frac{2}{1.2}\ln\left(1+1.2I^{1/2}\right)\right] \quad (27)$$

$$B_{12}^\gamma = 2\beta_{12}^{(0)} + \frac{2\beta_{12}^{(1)}}{4I}\left[1 - e^{-2I^{1/2}}\left(1 + 2I^{1/2} - 2I\right)\right] \quad (28)$$

The $\beta_{12}^{(0)}, \beta_{12}^{(1)},$ and C_{12}^γ are semi-empirical parameters, the values of which have been obtained from curve fitting of experimental data for various binary electrolyte solutions.

THE CONCEPT OF THE RELATIVE HUMIDITY OF DELIQUESCENCE

A solid particle transforms into an aqueous solution when the relative humidity reaches a specific level, characteristic for each salt. This is known as the relative humidity of deliquescence (DRH). The DRH is a function of temperature, and for a small temperature range can be calculated by (Wexler and Seinfeld, 1991):

$$ln \frac{DRH(T)}{DRH(T_o)} = -\frac{M_w m_s L_s}{1000R}\left(\frac{1}{T} - \frac{1}{T_o}\right) \quad (29)$$

where, T_o is the temperature in which the DRH is known (usually 298.15 K), M_w is the molecular weight of water, m_s is the molality of the saturated solution at temperature T_o, R is the universal gas constant, $L_s = \Delta H_{cr} - \Delta H_{aq}$ is the latent heat of fusion for the salt from a saturated solution, ΔH_{cr} is the standard heat of formation of the crystalline phase and ΔH_{aq} is the standard heat of formation of the species in aqueous solution. Tang and Munkelwitz (1993) proposed a more elaborate expression, but for moderate temperature ranges, they showed that Equation (29) is adequate.

The minimum relative humidity in which a multicomponent mixture can deliquesce is known as mutual deliquescence relative humidity (MDRH). This point is also known as the "eutonic point" (Tang and Munkelwitz, 1993) and corresponds to the mixture with a composition that minimizes water activity. Below this point, a solid phase is thermodynamically favored. Consequently, MDRH points can be used to determine whether an aqueous phase is present. The DRH of the mixture does not have a unique value, but is a function of mixture composition. At the MDRH, the aqueous phase is saturated with respect to all the salts. Therefore, it is the only RH in which an aqueous solution can coexist with a precipitate composed of all the aerosol salts. The system is said to be in a Mutual Deliquescence Region (MDR), when the relative humidity is:

$$MDRH(salt_1, salt_2, ... salt_n) \leq RH <$$
$$\min\left\{DRH_{salt_1}, DRH_{salt_2}, ... DRH_{salt_n}\right\}$$

Neglecting mutual deliquescence leads to the erroneous prediction of a dry aerosol for cases where the RH lies in a MDR. This potentially can affect the predicted role of aerosols, since the presence of aerosol water affects the partitioning of volatile species and particle size.

AVAILABLE THERMODYNAMIC EQUILIBRIUM MODELS

Several gas aerosol atmospheric equilibrium models have been developed with varying degrees of complexity and rigor in both the computational and the thermodynamic approaches. Bassett and Seinfeld (1983), developed EQUIL in order to calculate the aerosol composition of the ammonium-sulfate-nitrate-water aerosol system. They later introduced an improved version, KEQUIL, to account for the dependence of the partial vapor pressure on the spherical shape of the particles, the so-called Kelvin effect (Bassett and Seinfeld, 1984).

Another widely used model for the sulfate-nitrate-ammonia-water system is MARS (Saxena et al., 1986) that aimed at reducing the computational time while maintaining reasonable agreement with EQUIL and KEQUIL. MARS was developed for incorporation into larger aerosol models, so speed was a major issue. The main feature of MARS was the division of the whole aerosol species regime into subdomains, in order to minimize the viable species in each one. Since each domain contains fewer species than the entire concentration domain does, the number of equations solved is reduced, thus, speeding up the solution process. A major drawback of MARS is that it uses thermodynamic properties (equilibrium constants, activity coefficients) at 298.15 K, thus affecting the distribution of volatile species (nitrates) between the gas and the particulate phases, if calculations are done at a different temperature. All the simplifications rendered MARS about four hundred times faster than KEQUIL and sixty times faster than EQUIL.

The major disadvantage of the previous three models was the neglect of sodium and chloride species, which are major components of marine aerosols. These species were first incorporated into the SEQUILIB model (Pilinis and Seinfeld, 1987). SEQUILIB used a computational scheme similar to that of MARS. It also presented an algorithm for calculating the distribution of volatile species among particles of different sizes so that thermodynamic equilibrium is achieved between all the particles and the gas phase.

Recently, Kim et al. (1993) developed SCAPE, which implements a domain-oriented solution algorithm similar to that of SEQUILIB, but with updated thermodynamic data for the components. SCAPE also calculates the pH of the aerosol phase from the dissociation of all weak and strong acid/base components, and includes the temperature dependence of single salt deliquescence points using the expressions derived by Wexler and Seinfeld (1991). SCAPE embodied the main correlations available for calculating multi-component solution activity coefficients, and let the user select the one which should be used. SCAPE always attempts to solve for a liquid phase, by using SEQUILIB to calculate approximate concentrations that serve as a starting point for the iterative solution of the full equilibrium problem. Because of this approach, SCAPE can predict the presence of water, even at very low ambient relative humidities. In certain cases, the activity coefficients may lower the solubility product enough so that there is no solid precipitate predicted. There is no relative humidity "boundary" that could inhibit this, so a liquid phase may be predicted for relative humidities as low as 20%. There are two ways to solve this problem. Either certain assumptions must be made about the physical state of the aerosol at low relative humidities (like MARS and SEQUILIB), or the full minimization problem must be solved.

A different approach has been followed by Jacobson et al. (1996) in their model, EQUISOLV. The equilibrium concentrations are calculated by numerically solving each equilibrium equation separately, based on an initial guess for the concentrations. After solving each equation, the solution vector is updated and the new values are used to solve the remaining equations. This sequence is repeated over and over, until concentrations of all species converge. This open architecture makes it easy to incorporate new reactions and species. However, the general nature of the algorithm could potentially slow down the solution process, when compared to the domain approach used in MARS, SEQUILIB and SCAPE. Solubility products are used to determine the presence of solids. For this reason, EQUISOLV, just like SCAPE, can predict the presence of water even at very low relative humidities. Even for cases in which a solid aerosol is predicted, a negligible amount of water is assumed to exist in order to estimate the vapor pressure of species in the aerosol phase. Whilst this should not affect the results (because there is

too little water to affect the solution), additional computation is required, which could increase CPU time.

The most recent thermodynamic equilibrium model available to the scientific community is ISORROPIA. ISORROPIA models the sodium - ammonium - chloride - sulfate - nitrate - water aerosol system. The aerosol particles are assumed to be internally mixed, meaning that all particles of the same size have the same composition. The number of viable species (thus, the number of equilibrium reactions solved) is determined by the relative abundance of each species and the ambient relative humidity. A more detailed description of the equilibrium reactions and the solution procedure of ISORROPIA is presented elsewhere (Nenes et al., 1998). Special provision was taken in order to render ISORROPIA as fast and computationally efficient as possible. The equilibrium equations for each case were ordered and manipulated so that analytical solutions could be obtained for as many equations as possible. The number of iterations performed during the numerical solution largely determines the speed of the model. Hence, minimizing the number of equations needing numerical solution considerably reduces CPU time.

Adopting this approach, most cases could be solved using only one level of iteration. By comparison, SEQUILIB is more simplistic and potentially faster, but proves to be slower than ISORROPIA, mainly because SEQUILIB solves more equations numerically and uses nested iteration procedures of two (and sometimes three) levels when solving the equations. Another factor that speeds up ISORROPIA is the usage of precalculated tables, whenever possible. All major characteristics of the models described above are summarized in Table 1.

SUMMARY AND CONCLUSIONS

The theory on which, thermodynamic equilibrium models of atmospheric aerosols are based, has been presented, and the relevant equations have been described. The major available equilibrium models have been also introduced and their major characteristics listed. While individual methodologies, including binary activity coefficients, have been compared comprehensively in the past (Kim et al., 1993), there is a lack of an overall, detailed intercomparison of model performance. All models presented in this paper are scientifically sound, and should be tested with experimental data, collected under different atmospheric conditions. As a result, it would be greatly beneficial to the scientific community to undertake specific field experiments, for the collection of the necessary data against which these state of the art thermodynamic models could be tested.

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Table 1. Comparison of state of the art thermodynamic equilibrium aerosol models.

	KEQUIL	MARS	SEQUILIB
Multicomponent activity coefficients	K-M	Bromley	Bromley
Binary activity coefficients	K-M	Pitzer	Pitzer
Water activity	K-M	ZSR	ZSR
MDRH	NO	NO	NO
Kelvin effect	YES	NO	NO
Liquid components	H^+, NH_4^+, NO_3^-, HSO_4^-, SO_4^{2-}, H_2O	NH_3, H^+, NH_4^+, NO_3^-, HSO_4^-, SO_4^{2-}, H_2O	Na^+, Cl^-, H_2SO_4, H^+, NH_4^+, NO_3^-, HSO_4^-, SO_4^{2-}, H_2O
Solid components	$(NH_4)_2SO_4$, $(NH_4)_2SO_4$-$2NH_4NO_3$, $(NH_4)_2SO_4$-$3NH_4NO_3$, NH_4HSO_4, $(NH_4)_3H(SO_4)_2$, NH_4NO_3	$(NH_4)_2SO_4$, NH_4HSO_4, $(NH_4)_3H(SO_4)_2$, NH_4NO_3	$(NH_4)_2SO_4$, NH_4HSO_4, $(NH_4)_3H(SO_4)_2$, NH_4NO_3, NH_4Cl, $NaCl$, $NaNO_3$, $NaHSO_4$, Na_2SO_4
Gas components	NH_3, HNO_3, H_2SO_4, H_2O	NH_3, HNO_3, H_2O	NH_3, HNO_3, HCl, H_2O

	SCAPE	EQUISOLV	ISORROPIA
Multicomponent activity coefficients	Bromley, K-M, Pitzer	Bromley	Bromley
Binary activity coefficients	K-M	Pitzer	K-M
Water activity	ZSR	ZSR	ZSR
MDRH	NO	NO	YES
Kelvin effect	NO	NO	NO
Liquid components	Na^+, Cl^-, H_2SO_4, NH_3, H^+, NH_4^+, OH^-, NO_3^-, HSO_4^-, SO_4^{2-}, H_2O	Na^+, Cl^-, H_2SO_4, HNO_3, NH_3, H^+, NH_4^+, OH^-, NO_3^-, HSO_4^-, SO_4^{2-}, H_2O	Na^+, Cl^-, H_2SO_4, HNO_3, NH_3, H^+, NH_4^+, OH^-, NO_3^-, HSO_4^-, SO_4^{2-}, H_2O
Solid components	$(NH_4)_2SO_4$, NH_4HSO_4, $(NH_4)_3H(SO_4)_2$, NH_4NO_3, NH_4Cl, $NaCl$, $NaNO_3$, $NaHSO_4$, Na_2SO_4	$(NH_4)_2SO_4$, NH_4HSO_4, NH_4NO_3, NH_4Cl, $NaCl$, $NaNO_3$, $NaHSO_4$, Na_2SO_4	$(NH_4)_2SO_4$, NH_4HSO_4, $(NH_4)_3H(SO_4)_2$, NH_4NO_3, NH_4Cl, $NaCl$, $NaNO_3$, $NaHSO_4$, Na_2SO_4
Gas components	NH_3, HNO_3, HCl, H_2O	NH_3, HNO_3, HCl, H_2O	NH_3, HNO_3, HCl, H_2O

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