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Atmospheric Chemistry and Physics Discussions

Interactive comment on "A computationally efficient inorganic atmospheric aerosol phase equilibrium model (UHAERO)" *by* N. R. Amundson et al.

N. R. Amundson et al.

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S. Martin

A. Deliquescence

It is not necessary to present comparisons of phase diagrams since, as noted by Dr. Martin, the PSC model is generally considered to be the most accurate available. We agree that the work would benefit by presenting computing speed comparisons between UHAERO and other techniques for which we have access to the codes, and a longer discussion and three new tables have been added. Numbers 1–7 in the figures

are now defined.

B. Efflorescence

As noted by Dr. Martin, this paper presents the first attempt to treat efflorescence in a thermodynamic aerosol model.

II. Inaccurate Statements

1. Dr. Martin is correct that the value of the surface tension of the crystal germ has been computed from a measurement of the efflorescence RH and therefore experimental data underlie the model. The wording that suggests otherwise has been changed.

2. Dr. Martin suggests that homogeneous nucleation theory has yet to be rigorously tested to predict efflorescence and that the current model combined with the data of Schlenker et al. (2004) provides an opportunity to do so. We now note this. (The limitations of homogeneous nucleation theory are well-known. Nonetheless, this is the logical approach to start to build an algorithm for predicting crystallization).

3. The comments of Dr. Martin concerning the analysis in Cohen et al. (1987) are correct; the wording has been changed appropriately.

4. As noted above, the good agreement of predicted and observed crystallization behavior in Figure 13 is a result, at least in part, of the fact that the parameter values in the homogeneous nucleation theory have been determined based on experimental data. This point is now stressed.

5. Treatment of heterogeneous nucleation, e.g. letovicite can crystallize and then act as a nucleus for ammonium bisulfate to crystallize, is beyond the scope of the theory in the present paper.

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Anonymous Referee #2

1. Referee #2 suggests that somewhat more detail be given on the mathematical minimization method. We have added substantial material describing the method.

2. The method is applicable to any number of components. The code has been prepared so that it may be easily used by the community. This is now clear in the revision.

3. There is no need to test whether an initial guess using ZSR can improve performance.

4. The effect of curvature has not yet been included in the model. Inclusion of curvature can be readily handled by an extension of the method. This is now noted.

5. The current paper relates only to inorganic aerosol equilibrium. The reference to extended UNIQUAC in Table 1 in UHAERO refers to the organic/water version of UHAERO, which has not yet been reported in the literature.

6. Referee #2 comment here regards the treatment of organics and whether the current framework can easily accommodate the addition of an organic fraction. It turns out organics can easily be included in the framework, but the numerical minimization algorithm needed is entirely different. This will be the subject of our next paper.

Specific remarks

Section 1, Table 1: The EQSAM model has been added to Table 1. Lack of inclusion of this model was an oversight. It would not be appropriate to include Ming and Russell because that model addresses organic systems.

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Interactive Comment

Section 1, Paragraph 3: This comment relates again to organics, which will be the subject of a later paper.

Section 2: As noted above, curvature is neglected in the present model, and, as a result, the model has limitations for sub-100 nm particles.

Section 2, Paragraph 4: This point concerning the sensitivity of solid precipitation to the energies of formation of inorganic salts is now noted.

Section 2, Paragraph 6: Phase stability criteria are now stated.

Section 3, Paragraph 2: Choice of value for J_0 is discussed.

Section 3, Paragraph 4: The use of surface tension data is now discussed.

Section 4, Paragraph 1: Wording change has been made.

Section 4, Paragraph 3: The source of the energies of formation for the complex salts is now given.

Section 5: The discussion of the numerical performance of the method has been substantially increased, including three new tables.

Figures 1–11: The phase diagrams are identical to those predicted by AIM.

Anonymous Referee #1

1. Lack of inclusion of Metzger et al. (2002) was an oversight. This work is now included in the list of comparisons.

2. The effect of uncertainty in molecular volume of inorganic salts is now included.

3. It is suggested that the paper include comparisons of phase partitioning calculated with the present model with those calculated by SCAPE2 and ISORROPIA. The novel aspect of the present work is the efficient computational technique.

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The thermodynamic model used is AIM, which is generally regarded as the most accurate inorganic aerosol equilibrium model available. Evaluating the predictions of ISORROPIA, for example, versus those of AIM has been carried out previously and need not be reiterated here.

4. We agree with the referee that the paper would benefit by further comparisons of computation times versus other methods and these have now been added in Tables 2, 3 and 4. We reiterate that the power of the method presented here is that it allows use of the most rigorous thermodynamic model (therefore with no sacrifice of accuracy in the phase diagrams) at a level of computational speed that makes it a candidate for inclusion in three-dimensional CTMs.

5. A discussion of the overall uncertainties of phase partitioning in the inorganic systems is beyond the scope of the present work, and, as noted above, we defer discussion of organic system until future work.

A detailed point-by-point list of changes on the manuscript "A computationally efficient inorganic atmospheric aerosol phase equilibrium model (UHAERO)"

Page 2, Line 8:
.... The model computes deliquescence behavior without any a priori specification of the relative humidities of deliquescence. Also included in the model is a formulation based on classical theory of nucleation kinetics that predicts crystallization behavior. ...

Page 5, Line 16:
.... Thus, by neglecting curvature, the equilibrium of water between the gas and aerosol phases is defined by $a_w{=}RH$, where RH is the relative humidity in the atmosphere, expressed as a fraction. For a curved surface, i.e., that of sub-100 nm particles, the equilibrium partial pressure of a gas component i is greater than that required for a flat surface as described by the Kelvin equation (Seinfeld Pandis, 1998). Inclusion of

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curvature can be readily handled by an extension of the solution methods presented in the paper.

Page 6, Line 12:
.... The temperature dependence of the standard state chemical potential is calculated from

$$\mu_i^0(T) = T\left[\frac{\Delta G_f^0}{T_0} + \Delta H\left(\frac{1}{T} - \frac{1}{T_0}\right) + c_p\left(\ln\frac{1}{T} - \frac{T_0}{T} + 1\right)\right]$$

where ΔG_f^0 is the free energy of formation, ΔH the standard heat of formation, and c_p the heat capacity, of component i, all at T_0, a reference temperature. In conjunction with the PSC and ExUNIQUQAC models, we use the data sets of tabulated values of ΔG_f^0, ΔH and c_p for the the components in solid phases, as reported in Clegg et al. (1998a) and Thomsen Rasmussen (1999), where one can find analysis of the sensitivity of computed deliquescence behavior to such data sets. It shall be noted that the inclusion of the ExUNIQUAC model in the present paper is to illustrate that the UHAERO framework is applicable to any number of components with any activity coefficient model. The UHAERO code has been prepared so that it may be easily used by the community. ...

Page 7, Line 10, New Paragraph:
Traditional optimization algorithms applied (in Table 1) for the prediction of inorganic gas-aerosol equilibrium are often related to sequential quadratic programming methods for nonlinear programming, often combined with interior-point techniques for the handling of the non-negativity constraints on the concentrations of salts. One major difference that arises when nonlinear programming algorithms are applied as “black boxes” to solve gas-aerosol equilibrium problems is that the former typically employs generic linear algebra routines to solve linear systems arising in the algorithm, whereas for gas-aerosol equilibrium problems, specific sparse direct linear solvers that explore the special algebraic structure of gas-liquid and liquid-solid equilibrium relations have to be used in order to deal with the poor scaling of the concentrations in the computa-

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tion. It is known that a straight forward application of nonlinear programming algorithms is not effective, and that instead the iterates should be computed based on a primal-dual active set method. The numerical minimization technique of UHAERO is based on a primal-dual active-set algorithm, which is described in detail elsewhere (Amundson et al., 2005a,b). The algorithm is elucidated from the analysis of the algebraic structure of the Karush-Kuhn-Tucker (KKT) optimality conditions for the minimization of the Gibbs free energy. The reformulated KKT system is first derived to furnish the mass action laws in addition to the mass balance constraints (2). The mass action laws are in a logarithmic form. An immediate consequence of the logarithmic form is that the mass action laws in the primal-dual form are linear with respect to the dual variables, which represent the logarithmic values of activities for component species at equilibrium. In this primal-dual form, the mass action laws involving solid phases become linear inequality constraints that are enforced via the dual variables so that the solution remains dual feasible with respect to salt saturations. The concentrations of saturated salts are the Lagrange multipliers of the dual linear constraints that are active, thus can be eliminated from the KKT system by applying the so-called null-space method based on an *active set of solid phases*. Then, the algorithm applies Newton's method to the reduced KKT system of equations that is projected on the active set of solid phases to find the next *primal-dual* approximation of the solution. The active set method adds a solid salt when the components reach saturation and deletes a solid phase from the active set when its concentration violates the non-negativity constraint. The analysis of linear algebra with matrices of block structure provides information about the inertia of the so-called KKT matrices which arise in the Newton iterations. This information is used, as phase stability criteria, in line-search based methods to detect negative curvature and modify, if necessary, the second order information to ensure that the algorithm converges to a stable equilibrium rather than to any other first-order optimality point, such as a maximum, a saddle point, or an unstable local minimum. The iterates of concentrations follow a path that is infeasible with respect to the mass balance constraints in the first few iterations, then converge quadratically to the minimum of the

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Gibbs free energy.

Page 9, Line 8:
.... It shall be noted that Eq. (7) models only homogeneous nucleation, and can be extended straightforwardly to treat heterogeneous nucleation via the relation $\Delta G_{\mathrm{crit}}^{\mathrm{hete}} = \Delta G_{\mathrm{crit}} \psi(\theta)$, where $\psi(\theta)$ describes the efficacy of the heterogeneous nucleus in terms of θ, the contact angle formed between the germ and the substrate. However, the mire of details in modeling $\psi(\theta)$ according to classical heterogeneous nucleation theory is often difficult. Thus, we limit the scope of the theory in the present paper to the treatment of homogeneous nucleation. ...

Page 9, Line 18:
.... When the classical nucleation theory is used, the thermodynamic properties of the nucleus are assumed to be those of the bulk substance in question. For most salts of interest here, $c_{\mathrm{geom}} \approx 2$. In the present calculation, we employ the approximation $c_{\mathrm{geom},(\mathrm{NH_4})_3\mathrm{H}(\mathrm{SO_4})_2} = c_{\mathrm{geom},(\mathrm{NH_4})_2\mathrm{SO_4}}$ and take $c_{\mathrm{geom},(\mathrm{NH_4})_2\mathrm{SO_4}} = 2.072$ as in Table 3 of Cohen et al. (1987), where the value of c_{geom} for $(\mathrm{NH_4})_2\mathrm{SO_4}$ as 2.072 was obtained by assuming shape based upon bulk crystallography. The molecular density of the germ ρ_{germ}^0 can be obtained via $\rho_{\mathrm{germ}}^0 := \frac{1}{v_{\mathrm{germ}}^0}$, where v_{germ}^0 is the molecular volume. Here we take $v_{\mathrm{germ}}^0 = 85.307$ for $(\mathrm{NH_4})_2\mathrm{SO_4}$ and 148.99 for $(\mathrm{NH_4})_3\mathrm{H}(\mathrm{SO_4})_2$ as in Tang and Munkelwitz (1994).

Page 10, Line 8:
The results do not depend strongly on the pre-exponential factor and we follow Cohen et al. (1987) and choose $J_0 = 10^{30}$. ...

Page 11, Line 23:
... whereas $\sigma_{\mathrm{crystal/air}}$ is assumed to be a constant for a given crystal and is to be determined as a parameter based on one value of σ_{germ}, which, in turn, can be computed from one measurement of the efflorescence RH of the corresponding crystalline salt. Cohen et al. (1987) correlated, based on classical nucleation theory,

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the value for the surface tension of salt $(NH_4)_2SO_4$ in the solute mixture of ASR=2 (ASR: ammonium-sulfate-ratio) with measured efflorescence RH. The computed value $\sigma_{(NH_4)_2SO_4}(\mathrm{ASR}{=}2){=}0.0368$ kg s^{-2}, reported in Cohen et al. (1987), is used to ....

Page 12, Line 13, New Paragraph:
The major advantage of classical nucleation theory is that the expectation time of the crystallization of metastable solutions is conveniently related to the thermodynamic properties of the nucleus such as the shape c_{geom}, molecular volume v^0_{germ} and surface tension σ_{germ}. However, major conceptual shortcomings also exist in assuming bulk values of c_{geom}, v^0_{germ} and σ_{germ} are relevant at the cluster level, where the nucleus consists of a statistically small number of molecules. In fact, we consider here classical nucleation theory as a semi-empirical correlation, and we calibrate the values of c_{geom}, v^0_{germ} and $\sigma_{\mathrm{crystal/air}}$, as parameters for the calculation of the crystallization time τ_{nucl} in Eq. (10), so that the computed efflorescence RH matches the measured value. Any extrapolations beyond the domain of calibration needs be done with caution. The application of classical nucleation theory to predict efflorescence has yet to be rigorously tested and the current model combined with measurements such as the data reported in Schlenker et al. (2004) provides an opportunity to do so.

Page 13, Line 2:
The inorganic system that is ...

Page 15, line 17:
..., where the liquid phase is labeled by L, and where, as in Figure 1, the seven possible solid phases are labeled by A though G. ...

Page 16, Line 3, New Paragraph:
Figure 12 depicts the surface tension $\sigma_{\mathrm{liquid/air}}$, computed based on Eq. (12), for the binary electrolyte aqueous solution $(NH_4)_2SO_4/H_2SO_4/H_2O$ at 298.15 K. The activity coefficient calculation is carried out using the ExUNIQUAC model (Thomsen and

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Rasmussen, 1999). The parameters $\Gamma_i^{w_0}$ and K_i, $i \in \{1,2\}=\{(NH_4)_2SO_4, H_2SO_4\}$, in Eq. (12) are determined from Eq. (11) by correlating the surface tension of the corresponding single electrolyte aqueous solutions against the measurements of Martin et al. (2000) and Korhonen et al. (1998). The original values of $\Gamma_i^{w_0}$ and K_i as reported in Li and Lu (2001) are not suitable for the present calculation, as they were calibrated mostly with measurements of low concentrated electrolyte solutions and were obtained based on a different activity coefficient model. The accuracy of the surface tension calibration based on Li and Lu's formula, e.g., Eq. (12), depends largely on the applicability of activity coefficient models to supersaturated aqueous solutions of highly concentrated and mixed electrolytes. Most of the models that predict the activity coefficients of multicomponent aqueous solutions are empirical, or semi-empirical, and typically calibrated with activity measurements for multicomponent systems that are mostly available for relatively low ionic activities. As such, any application of current activity coefficient models to supersaturated aqueous solutions of highly concentrated and mixed electrolytes is an extrapolation beyond the domain of calibration, thus should be viewed with caution. In fact, as one specific example of such extrapolation, we were unable to calibrate model parameters in Eq. (12) to obtain a satisfactory calculation of the surface tension $\sigma_{\mathrm{liquid/air}}$ for the ternary electrolyte aqueous solution $(NH_4)_2SO_4/H_2SO_4/NH_4NO_3/HNO_3/H_2O$; high deviations of the computed values of surface tension from the measurements of Martin et al. (2000) occur at supersaturated solutions that are nitrate rich. Thus, in order to apply the current model to predict crystallization behavior in a multicomponent solution, there is a need to develop/calibrate activity coefficient models that are capable to predict accurately activity coefficients of supersaturated multicomponent aqueous solutions.

Page 17, Line 3:
... in the nature logarithmic scale, $\ln \tau_{\mathrm{nucl}}$, ...

Page 17, Line 7:
.... It shall be noted that the good agreement of the predicted and observed efflores-

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cence RH in Figure 13 is in part due to the AS and LET curves are forced, respectively, to intersect with the observation curve at ASR =2 and 1.5. This is a result of the fact that the parameter values $\sigma_{\mathrm{crystal/air}}$ for AS and LET in the homogeneous nucleation theory have been determined based on a measurement of the efflorescence RH at these two ASR points.

Page 17, Line 13, New Paragraph:
It shall be also noted that the present model treats only homogeneous nucleation and, as a result, there is no possibility to predict the crystallization of ammonium bisulfate and ammonium nitrate. In contrast, the measurements of Schlenker et al. (2004) show that these salts do crystallize by heterogeneous nucleation once another crystal has formed by homogeneous nucleation. Thus, a rigorous validation of the UHAERO framework through comparisons to the experimental data of Martin et al. (2003) and Schlenker et al. (2004) in the ammonium-sulfate-nitrate space would require the treatment of heterogeneous nucleation, a topic that is beyond the scope of the present paper and that will be a subject of the future research.

Page 17, Line 22, Section 5 (rewritten):
The initialization of UHAERO has two modes depending on the circumstance of its application: (a) a so-called cold start, in which no a priori information is available and the system is initialized as an infinitely dilute solution, or (b) a warm-start, in which a convergent solution of a neighbor state is available to initialize the system; this is the case when applying it in conjunction with a 3-D chemical transport model. The computational cost for Case (1) (i.e., the water content is specified) is estimated with the model runs for generating phase diagrams. For the contour plots (for $Y{=}0.85$) shown in Figure 14, a uniform grid with $\frac{1}{2}n(n-1)$ ($n{=}100$) (interior) points on the unit triangle is used. When the warm start strategy is applied for the liquid-solid equilibrium calculations where the model run for the (i,j) point is initialized with the solution of the (i,j-1) point, the elapsed time is 0.52 s (or 0.20 s) for 4950 UHAERO-PSC (or UHAERO-ExUNIQUAC) runs on a Linux PC equipped with Intel(R) Pentium(R) 4

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3.20 GHz processor. It requires an average 3.45 (or 3.37) Newton iterations per grid point for UHAERO-PSC (or UHAERO-ExUNIQUAC) runs with a stopping criterion for convergence being that the square-root of the residuals does not exceed 10^{-8}. If a cold start is used for generating contours, the average number of Newton iterations per grid point required for the convergence is 15.1 (or 12.75) for UHAERO-PSC (or UHAERO-ExUNIQUAC) runs. The computational cost for Case (2) (RH is fixed) is estimated with the model runs for the generation of the contour plots in the (X, RH) coordinate (for Y=0.85) as shown in Figure 4. By using a uniform grid of $(n-1)\times(n-1)$ (interior) points (n=100) on the unit square and applying the same warm-start strategy, it takes 1.1 s (or 0.47 s) for 9801 UHAERO-PSC (or UHAERO-ExUNIQUAC) runs, a time that is doubled in comparison with Case (1) due to the doubling of the grid points. The average Newton iterations per grid point for the convergence solution is 3.41 (or 3.24) for UHAERO-PSC (or UHAERO-ExUNIQUAC) runs. The computation times quoted above are those for generation of the entire phase diagram of 9801 points. If implemented in a 3-D atmospheric model with, say, 50×50×10=25 000 grid cells, then the total computing time needed per time step for the thermodynamic calculation is estimated to be about 2.9 s (or 1.2 s) for UHAERO-PSC (or UHAERO-ExUNIQUAC) runs. Moreover, this corresponds to a very strict convergence criterion that the square root of the residuals is less than 10^{-8}. The same efficiency is achieved in either mode of application; there is no need, for example, to iterate on the water content as is required in several other models.

When UHAERO is applied for the gas-aerosol equilibrium calculations, the computational time and the number of Newton iterations are slightly increased, but still are of the same order as in the case of the liquid-solid calculations. Table 2 lists the average numbers of Newton iterations per grid point for a convergence solution when applying UHAERO with various model configurations for the reconstruction of a phase diagram. Table 3 shows average CPU-times (μs) per Newton iteration and average CPU-percentage per Newton iteration for activity coefficient calculations when applying UHAERO for the reconstruction of a phase diagram in both the (X, RH) and (X,

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Z) coordinates with Y=0.85. The calculations are performed on two different computer architectures: a Linux PC equipped with 32-bit Intel(R) Pentium(R) 4 3.20GHz processor and a Linux PC equipped with 64-bit AMD(R) Opteron(R) 2.39GHz processor. The CPU times of UHAERO-PSC runs are dominated by the PSC model calculations of activity coefficients and the average CPU-percentages for activity coefficient calculations range from 54.1% to 70.0%. Since the ExUNIQUAC model does not consider ternary interactions, it is more efficient for activity coefficient calculations compared to the PSC model, and takes from 21.8% to 34.5% of the total CPU-times of UHAERO-ExUNIQUAC runs. The overall CPU time of UHAERO-ExUNIQUAC is 1.7 faster than that of UHAERO-PSC for gas-aerosol equilibrium calculations; in the case of liquid-solid equilibrium calculations, a speed-up factor of 2.5 is observed. Based on the widespread application of ISORROPIA, the examination of the model performance of UHAERO against that of ISORROPIA over an extended composition, temperature, and RH domain is necessary. The performance and advantages of ISORROPIA over the usage of other thermodynamic equilibrium codes is assessed in Nenes et al. (1998); Ansari and Pandis (1999). Since the evaluation of the predictions of ISORROPIA versus those of AIM has been carried out previously and since AIM uses the same activity coefficient model as UHAERO-PSC, we focus here the computing speed comparisons between UHAERO and ISORROPIA. Table 4 compares the average CPU-times (μs) per grid point and the average number of iterations per grid point when applying UHAERO (in the warm-start mode) and ISORROPIA for "reverse problems" on a uniform grid of $(n-1) \times (n-1)$ ($n = 100$) (interior) points on the unit square in the (X, RH) coordinate with Y=0.85. The calculations of "reverse problems", in which known quantities are temperature, relative humidity and the aerosol phase concentrations, are needed in detailed models of aerosol dynamics (Pilinis et al., 2000). The CPU-times for ISORROPIA runs are measured for two different sets of convergence criteria as in Makar et al. (2003). The "High" runs use convergence criteria appropriate for applications in which accuracy is more important than the net processing time. The "Low" runs use convergence criteria appropriate for applications in which processing speed

has a greater priority than the details of solution accuracy. It can be observed that the overall speed of UHAERO is comparable to that of ISORROPIA, thus is appropriate for the inclusion of UHAERO in 3-D chemical transport models.

Page 20, Line 10:
.... The model includes a first-principles calculation of deliquescence behavior. The first attempt to treat efflorescence in a thermodynamic aerosol model based on liquid-solid nucleation theory is also presented. ...

Page 22, Lines 10, 26, 30; Page 23, Lines 9, 22; New References:
Makar, P. A., Bouchet, V. S., and Nenes, A.: Inorganic chemistry calculations using HETV - vectorized solver for $SO_4^{2-}/NO_3^-/NH_4^+$ system based on the ISORROPIA algorithms, Atmos. Environ., 37(16), 2279–2294, doi:10.1016/S1352-2310(03)00074-8, 2003.

Metzger, S., Dentener, F., Pandis, S., and Lelieveld, J.: Gas/aerosol partitioning: 1. A computationally efficient model, J. Geophys. Res., 107 (D16), 4312, doi:10.1029/2001JD001102, 2002.

Pilinis, C., Capaldo, K. P., Nenes, A., and Pandis, S. N.: MADM - a new multicomponent aerosol dynamics model, Aerosol Sci. Tech., 32(5), 482–502, 2000.

Schlenker, J. C., Malinowski, A., Martin, S. T., Hung, H., and Rudich, Y.: Crystals formed at 293 K by aqueous sulfate-nitrate-ammonium-proton aerosol particles, J. Phys. Chem., 108, 9375–9383, 2004.

Trebs, I., Metzger, S., Meixner, F. X., Helas, G., Hoffer, A., Rudich, Y., Falkovich, A. H., Moura, M. A. L., da Silva, R. S., Artaxo, P., Slanina, J., Andreae, M. O.: The $NH_4^+ - NO_3^- - Cl^- - SO_4^{-2} - H_2O$ aerosol system and its gas phase precursors at a pasture site in the Amazon Basin: How relevant are mineral cations and soluble organic acids? J. Geophys. Res., 110, D07303, doi:10.1029/2004JD005478, 2005

Page 25, Table 1:

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... EQSAM, $NH_4^+/Na^+/K^+/Ca^{2+}/Mg^+/NO_3^-/SO_4^{-2}/Cl^-$, Parameterization of activity coefficient-RH relationship, No iterations required. ...
[2] ...; EQSAM (Metzger et al.,2002; Trebs et al.,2005); ...

Pages 26, 27, 28; New Tables:
Table 2. Average number of Newton iterations per grid point (UHAERO)[1].

Table 3. Average CPU-times (μs) per Newton iteration and average CPU-percentage per Newton iteration for activity coefficient calculations (UHAERO)[1].

Table 4. Average CPU-times ($\mu\ s$) per grid point and average number of iterations per grid point (UHAERO vs. ISORROPIA)[1].

Pages 32,34,36,38; Caption of Figs. 4, 6, 8, 10:
.... For the regions numbered as 1 through 7, the existing phases at equilibrium are L+A+E, L+B+E, L+B+F, L+B+D, L+B+G, L+B+C, and L+C+G, respectively. ...

.... For the regions numbered as 1 through 3, the existing phases at equilibrium are L+A+B, L+B+D, and L+B+G, respectively. ...

.... For the regions numbered as 1 and 2, the existing phases at equilibrium are L+A+E and L+D+F, respectively. ...

.... For the regions numbered as 1 through 5, the existing phases at equilibrium are L+A, L+A+E, L+E, L+E+F, and L+B+D, respectively. ...

Page 40, New Figure:
Fig. 12. Surface tension for the binary electrolyte aqueous solution $(NH_4)_2SO_4/H_2SO_4/H_2O$ at 298.15 K. Labels on the contours (—) present the surface tension values $\sigma_{\mathrm{liquid/air}}$ (dyn/cm), computed based on Li & Lu's mixing rule (Li and Lu, 2001).

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