A Primal-Dual Active-Set Algorithm for Chemical Equilibrium Problems Related to Modeling of Atmospheric Inorganic Aerosols [1]

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Abstract. A general equilibrium model for multiphase multicomponent inorganic atmospheric aerosols is proposed. The thermodynamic equilibrium is given by the minimum of the Gibbs free energy for a system involving an aqueous phase, a gas phase and solid salts. A primal-dual algorithm solving the *Karush-Kuhn-Tucker* conditions is detailed. An active set/Newton method permits to compute the minimum of energy and track the presence or not of solid salts at the equilibrium. Numerical results show the efficiency of our algorithm for the prediction of multiphase multireaction chemical equilibria.

Key Words. Inorganic aerosols, thermodynamic equilibrium, constrained minimization, primal-dual methods, active sets.

1 Introduction

Over the last two decades, a series of thermodynamic modules, such as EQUIL (Ref. 1), MARS (Ref. 2), SEQUILIB (Ref. 3), SCAPE (Refs. 4-5), SCAPE2 (Refs. 6-7), EQUISOLV II (Refs. 8–10), and ISORROPIA (Refs. 11-12), has been developed in the atmospheric modeling community to predict the phase transition and multistage growth phenomena of inorganic aerosols. These modules calculate the composition of atmospheric aerosols by *solving a set of nonlinear algebraic equations* derived from chemical equilibrium relations. One of the most challenging parts is the prediction of the partitioning of the inorganic aerosol components between aqueous and solid phases. By *relying on a priori and often incomplete knowledge of the presence of solid phases* at a certain relative humidity and overall composition (information extracted from empirical data), these modules often fail to accurately predict the phase state and composition and the multistage growth phenomena of inorganic aerosols (Refs. 13-14).

On the other hand, thermodynamic models that are based on the *minimization of the Gibbs free energy*, such as GFEMN (Ref. 14) and AIM (Refs. 15–19), implicitly predict phase transition and multistage aerosol growth without any *a priori* knowledge of the behavior of inorganic aerosols. However, such direct minimization of the Gibbs free energy is computationally intensive making its use in 3D air quality models infeasible (Refs. 13-20).

In this paper, a *primal-dual active set* algorithm for the efficient and ac-

curate prediction of the phase transition and multistage growth phenomena of inorganic aerosols is presented. The mathematical framework for modeling solid-liquid equilibrium reactions is based on the *canonical stoichiometry* of inorganic aerosols (Ref. 21). The canonical form is elucidated from the analysis of the algebraic structure of aqueous electrolyte solution system and the Karush-Kuhn-Tucker (KKT) conditions for the constrained minimization of the Gibbs free energy. The concentrations of solid species in solid-liquid equilibrium are interpreted as the Lagrange multipliers of dual linear inequality constraints. This primal-dual relation is the key for the development of our primal-dual active set algorithm, whose principal features can be summarized as follows.

The algorithm applies Newton's method to the reduced KKT system of equations that is projected on an *active set of solid phases* to find the next *primal-dual* approximation of the solution. The *active set method* permits us to add/delete salts to/from a working set of *saturated salts* until the equilibrium set of solid phases is obtained. The linear inequality constraints are enforced on the dual variables such that the solution remains dual feasible with respect to the solid constraints, until an inequality constraint becomes active at an iteration and the active set is modified by adding a saturated salt into it. The concentrations of the saturated salts in the active set are the Lagrange multipliers of the dual active constraints so that their non-negativeness is enforced by deleting a saturated salt from the active set when its concentration becoming negative.

A second order *stability criterion* is implemented by keeping the reduced Hessian of the Gibbs free energy positive definite so that the algorithm converges to a stable equilibrium (local minimum) rather than any other first order optimality point such as a maximum or a saddle point. To avoid the non-positiveness and poor-scaling of the concentrations in the computation, a logarithmic change of variables is performed so that the 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 Gibbs free energy.

The structure of this paper is the following: in Section 2, the steps of the mathematical modeling of inorganic aerosols are presented. In Section 3, the optimization problem is derived and modified until obtaining a suitable formulation from both the chemical and mathematical points of view. Then, in Section 4, an active set/Newton method is detailed for solving this minimization problem. Numerical results are presented in Section 5 to illustrate

the efficiency of our approach. Section 6 consists in the conclusions.

2 Modeling of Inorganic Aerosols

2.1 Chemical Equilibrium Problem

The multi-phase and multi-reaction chemical equilibrium for a closed inorganic aerosol system at constant temperature and pressure and a specified element-abundance feed vector $\hat{b}$ is the minimization problem

$$\begin{aligned} \min \quad & G(n_l, n_g, n_s) = n_l^T \mu_l + n_g^T \mu_g + n_s^T \mu_s, && \text{(1a)} \\ \text{s. t.} \quad & n_l > 0, \quad n_g > 0, \quad n_s \geq 0, && \text{(1b)} \\ & \hat{A}_l n_l + \hat{A}_g n_g + \hat{A}_s n_s = \hat{b}, && \text{(1c)} \end{aligned}$$

where $n_\alpha \in \mathbb{R}^{m_\alpha}$, $\mu_\alpha \in \mathbb{R}^{m_\alpha}$ and $\hat{A}_\alpha \in \mathbb{R}^{m_e \times m_\alpha}$ are the concentration vector, the chemical potential vector and the element-based formula matrix for the species set $\alpha = l, g, s$ respectively. The subscripts l, g, s denote the liquid, gas and solid phases respectively. Here m_e denotes the number of elements in the system and m_α denotes the number of species in species set α. Let $G_\alpha = n_\alpha^T \mu_\alpha$ denote the Gibbs free energy related to the phase α. The aqueous and gas phases are assumed to exist at the equilibrium.

Remark 2.1. Let $\mathcal{X}_1, \ldots, \mathcal{X}_m$ denote the m chemical species expected to be present in the system, whose molecular structures are described by the *formula vectors* $\hat{a}_1, \ldots, \hat{a}_m$, defined by

$$\mathcal{X}_j = \sum_{i=1}^{m_e} \hat{a}_{ij} \mathcal{E}_i, \quad \forall j = 1, \ldots, m, \tag{2}$$

where the species are constituted as the linear combinations of the m_e *basic elements* $\mathcal{E}_1$, ..., $\mathcal{E}_{m_e}$.

Let $\mathcal{E}_{m_e}$, the last basic element in (2), be the *electronic charge*. Then, the first $m_e - 1$ rows of $\hat{A}_g$, $\hat{A}_l$ and $\hat{A}_s$ are non-negative, the last rows of $\hat{A}_g$ and $\hat{A}_s$ are zeros, and the last equation in the element-balance constraints of (1) describes the *electro-neutrality* of the system.

Let $\mathcal{I}$ be the index set of the species in the system and $m := |\mathcal{I}|$. The index set $\mathcal{I}$ can be split into $\mathcal{I}_g$, $\mathcal{I}_l$ and $\mathcal{I}_s$, with $m_g := |\mathcal{I}_g|$, $m_l := |\mathcal{I}_l|$,

$m_s := |\mathcal{I}_s|$, according to the gas, aqueous and solid phases, respectively. The element-based formula matrices in (1) are defined by $\hat{A}_\alpha = (\hat{a}_j)_{j\in\mathcal{I}_\alpha}$ for $\alpha = g, l, s$. The chemical potential vectors μ_α, $\alpha = g, l, s$, in (1) are given by

$$\mu_g = \mu_g^0 + RT \log a_g, \tag{3}$$

$$\mu_l = \mu_l^0 + RT \log a_l, \tag{4}$$

$$\mu_s = \mu_s^0, \tag{5}$$

where R is the universal gas constant and T is the system temperature. In (3), μ_g^0 is the standard chemical potential vector of the gas species at a pressure of 1 atm and the system temperature, and a_g is the activity vector of the gas species. This activity vector is given by

$$a_g = f_g \tag{6}$$

where f_g is the fugacity vector of the gas species and is given by $f_g = (p_{1\text{ atm}}/n_{\text{air}})n_g$, where $p_{1\text{ atm}}$ is the ratio $P/(1\text{ atm})$ with P denoting the system pressure and n_{air} is the total number of moles of air in the system.

In (4), μ_l^0 is the standard chemical potential vector of the aqueous species at the system temperature and pressure, and a_l is the activity vector of the aqueous phase that is predicted via an activity coefficient model. In (5), μ_s^0 is the standard *constant* chemical potential vector of the solid species at the system temperature and pressure.

Let us denote by $\mathbb{R}_{++}$ the strictly positive real numbers. Note that the chemical potential vector μ_l is defined as the gradient of the Gibbs free energy of the aqueous phase: $G_l : \mathbb{R}_{++}^{m_l} \to \mathbb{R}_+$, so that, for all $n_l > 0$,

$$\mu_l = \nabla G_l(n_l).$$

The first-order homogeneity of G_l is the basis for the relation

$$G_l(n_l) = n_l^T \mu_l,$$

and the Gibbs-Duhem equations:

$$\nabla^2 G_l(n_l) n_l = 0, \tag{7}$$

equivalently

$$(\nabla \mu_l)\, n_l = 0 \text{ or } (\nabla \log a_l)\, n_l = 0.$$

The respective Hessian matrices are given by

$$H_l = \nabla^2 G_l(n_l), \quad H_g = \mathrm{diag}(1/n_g) \text{ and } H_s = 0.$$

The above Gibbs-Duhem relations are used in the derivation of the optimality conditions for problem (1) in Section 3.

3 Description of the Problem and Optimality Conditions

3.1 KKT System and Canonical Stoichiometry

Assuming that the aqueous and gas phases are present at equilibrium, the solution of the chemical equilibrium (1) is characterized by the Karush-Kuhn-Tucker (KKT) system of the first order necessary optimality conditions, see *e.g.* (Ref. 22):

$$\mu_l + \hat{A}_l^T \lambda = 0, \tag{8a}$$
$$\mu_g + \hat{A}_g^T \lambda = 0, \tag{8b}$$
$$\mu_s + \hat{A}_s^T \lambda \geq 0, \quad n_s \geq 0, \quad n_s^T(\mu_s + \hat{A}_s^T \lambda) = 0, \tag{8c}$$
$$\hat{A}_l n_l + \hat{A}_g n_g + \hat{A}_s n_s = \hat{b}. \tag{8d}$$

The KKT system (8) is referred to as the *non-stoichiometric form* of the equilibrium conditions. These conditions can be expressed in an alternative and computationally more relevant form, the *stoichiometric form*, by extracting a set of component species from the aqueous species as described in the sequel.

To ensure the feasibility of solid-liquid and gas-liquid equilibrium reactions in (1), the species sets $\mathcal{I}_\alpha$, $\alpha = g, l, s$, in the system are assumed to be consistent in the sense that

$$\mathrm{range}(\hat{A}_l, \hat{A}_g, \hat{A}_s) = \mathrm{range}(\hat{A}_l). \tag{9}$$

The consistency (9) requires that all the gas and solid species in the system can be generated as a linear combination of the aqueous species. It is also assumed that $m_l > m_e$, *i.e.*, the number of the aqueous species is larger than the number of the elements. Let m_c ($\leq m_e$) be the rank of $\hat{A}_l$. The next

step is to select the m_c chemical species which play the role of components of the system. Thus, the set $\mathcal{I}_c$ ($\subset \mathcal{I}_l$) is a set of m_c aqueous species whose corresponding formula vectors $\hat{a}_j$ are linearly independent. These species are called the *components*. Let $\hat{A}_c := (\hat{a}_i)_{i\in\mathcal{I}_c} \in \mathbb{R}^{m_e\times m_c}$ be the formula matrix for the components. If $m_c = m_e$, *i.e.*, $\hat{A}_c$ is of full row rank, then $\hat{A}_c^{-1}$ exists; otherwise, the pseudoinverse of $\hat{A}_c$ is denoted by

$$\hat{A}_c^{-1} := (\hat{A}_c^T \hat{A}_c)^{-1} \hat{A}_c^T \in \mathbb{R}^{m_c\times m_e}.$$

The vector $\hat{b} \in \mathbb{R}^{m_e}$ is assumed to belong to range($\hat{A}_l$). Let $\mathcal{I}_n$ be the set of the remaining $m_n = m_l - m_c$ aqueous species with the formula matrix $\hat{A}_n := (\hat{a}_i)_{i\in\mathcal{I}_n} \in \mathbb{R}^{m_e\times m_n}$. These species are called the non-components. Let us define

$$A_\alpha = (a_{ij}^\alpha) := \hat{A}_c^{-1}\hat{A}_\alpha, \quad \text{for } \alpha = c, n, g, s,$$

the *component-based* formula matrix for species set α. Notice that $A_c = I_{m_c}$.

Remark 3.1. The matrices A_α, $\alpha = c, n, g, s$ are also called the *canonical stoichiometric matrices* as their rows are formed of the stoichiometric coefficients associated to the *canonical chemical equilibrium reactions*:

$$\mathcal{X}_j \leftrightarrows \sum_{i\in\mathcal{I}_c} a_{ij}^\alpha \mathcal{X}_i, \quad \forall j \in \mathcal{I}_\alpha, \quad \text{for } \alpha = c, n, g, s. \tag{10}$$

The corresponding *canonical equilibrium-constant* vector $k_\alpha = (k_j^\alpha)_{j\in\mathcal{I}_\alpha}$ is defined by

$$-RT \log k_\alpha := A_\alpha^T \mu_c^0 - \mu_\alpha^0, \quad \text{for } \alpha = c, n, s, g \tag{11}$$

and expresses the relation between the chemical potentials. Note that $\log k_c = 0$.

Let $b = \hat{A}_c^{-1}\hat{b}$ be the component-based feed vector, and $n_c \in \mathbb{R}_+^{m_c}$ and $n_n \in \mathbb{R}_+^{m_n}$ be the concentration vector of the components and non-components, respectively. Then, the element balance equations in (1) can be replaced by the component balance equations

$$n_c + A_n n_n + A_g n_g + A_s n_s = b. \tag{12}$$

The Gibbs free energy in the chemical equilibrium problem (1) can also be reformulated by replacing the chemical potentials in terms of activities and equilibrium constants via (3)-(5) and (11), and by taking into account (12):

$$\begin{aligned} G(n_l, n_g, n_s) = b^T \mu_c^0 + RT \Big(& n_c^T \log a_c \\ & + \; n_n^T (\log a_n + \log k_n) + n_g^T (\log a_g + \log k_g) + n_s^T \log k_s \Big). \end{aligned}$$

Let $c_{\mathrm{f}} > 0$ be a characteristic quantity of the feed vector b (for instance $c_{\mathrm{f}} = e^T b$). Let us define the adimensional feed vector $\tilde{b}$, the adimensional concentration vectors $\tilde{n}_\alpha$, and the adimensional Gibbs free energy $\tilde{G}$ by

$$\begin{aligned} & \tilde{b} = \frac{1}{c_{\mathrm{f}}} b, \quad \tilde{n}_\alpha = \frac{1}{c_{\mathrm{f}}} n_\alpha, \quad \alpha = c, n, g, s, \\ & \tilde{G} = \tilde{n}_c^T \log a_c + \tilde{n}_n^T (\log a_n + \log k_n) + \tilde{n}_g^T (\log a_g + \log k_g) + \tilde{n}_s^T \log k_s. \end{aligned}$$

The problem (1) can be written in the *adimensional canonical stoichiometric form* (dropping the tilde in the notation):

$$\begin{aligned} \min \quad & G(n_l, n_g, n_s) = n_c^T \log a_c + n_n^T (\log a_n + \log k_n) && \text{(13a)} \\ & \qquad + n_g^T (\log a_g + \log k_g) + n_s^T \log k_s, && \text{(13b)} \\ \text{s. t.} \quad & n_l = \begin{pmatrix} n_c \\ n_n \end{pmatrix} > 0, \quad n_g > 0, \quad n_s \geq 0, && \text{(13c)} \\ & n_c + A_n n_n + A_g n_g + A_s n_s = b. && \text{(13d)} \end{aligned}$$

The KKT system of (13) can be written in the *primal-dual canonical stoichiometric form*:

$$\log a_c + \lambda = 0, \tag{14}$$
$$\log a_n + A_n^T \lambda = -\log k_n, \tag{15}$$
$$\log a_g + A_g^T \lambda = -\log k_g, \tag{16}$$
$$\log k_s + A_s^T \lambda \geq 0, \quad n_s \geq 0, \tag{17}$$
$$n_s^T (\log k_s + A_s^T \lambda) = 0, \tag{18}$$
$$n_c + A_n n_n + A_g n_g + A_s n_s = b. \tag{19}$$

Remark 3.2. The above KKT system furnishes the mass action laws (14)-(18) in addition to the mass balance constraints (19). 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 (14)-(18) are linear with respect to the dual variable λ.

3.2 Chemical Equilibrium Problem at Fixed Relative Humidity

In atmospheric aerosol thermodynamic calculations, the ambient relative humidity (RH) is usually treated as a known constant. Then the water deserves a special treatment in the system and is isolated from the other components. This is described in the following remark.

Remark 3.3. The ratio p_w/p_w^0 between the water partial pressure p_w and the saturation vapor pressure p_w^0 is defined to be equal to the RH expressed in the 0 to 1 scale. From the definition of $\log a_{\mathrm{H_2O(g)}}$ in (6) and $\log k_{\mathrm{H_2O(g)}}$ in (11), it follows that

$$\log a_{\mathrm{H_2O(g)}} + \log k_{\mathrm{H_2O(g)}} = \log p_w - \log p_w^0 = \log \mathrm{RH}, \qquad \text{with } \mathrm{RH} = \frac{\mathrm{RH}_{100}}{100}.$$

Let the gas/particle partitioning of the total amount of H_2O be

$$n_{\mathrm{H_2O(total)}} = n_{\mathrm{H_2O(g)}} + n_{\mathrm{H_2O(pm)}}, \tag{20}$$

where the subscript *pm* denotes the particulate matter, *i.e.* the water under particulate form.

In light of Remark 3.3, the total feed vector b is split into the no-water part $\bar{b}$ and the water part as follows:

$$b = \bar{b} + n_{\mathrm{H_2O(total)}} a_{\mathrm{H_2O}}, \tag{21}$$

where $a_{\mathrm{H_2O}}$ is the formula vector for $\mathrm{H_2O}$. Let $\bar{\mathcal{I}}_g = \mathcal{I}_g \setminus \{\mathrm{H_2O(g)}\}$ be the index set of gas species excluding the water vapor, and $\bar{n}_g = (n_{g,j})_{j \in \bar{\mathcal{I}}_g}$ and $\bar{A}_g = (a_{g,j})_{j \in \bar{\mathcal{I}}_g}$ be the corresponding concentration vector and formula matrix, respectively. Then, by combining (20) and (21) with the relations $A_g n_g = \bar{A}_g \bar{n}_g + n_{\mathrm{H_2O(g)}} a_{\mathrm{H_2O}}$ and $n_g^T(\log a_g + \log k_g) = \bar{n}_g^T(\log \bar{a}_g + \log \bar{k}_g) + n_{\mathrm{H_2O(g)}} \log \mathrm{RH}$, the (adimensional) component balance equations in (13) can be written as

$$n_c + A_n n_n + \bar{A}_g \bar{n}_g + A_s n_s = \bar{b} + n_{\mathrm{H_2O(pm)}} a_{\mathrm{H_2O}},$$

and the (adimensional) Gibbs free energy in (13) can be written as

$$\begin{aligned} G(n_l, \bar{n}_g, n_s, n_{\mathrm{H_2O(pm)}}) &= n_c^T \log a_c + n_n^T(\log a_n + \log k_n) \\ &+ \bar{n}_g^T(\log \bar{a}_g + \log \bar{k}_g) + n_s^T \log k_s - n_{\mathrm{H_2O(pm)}} \log \mathrm{RH} \\ &+ n_{\mathrm{H_2O(total)}} \log \mathrm{RH}, \end{aligned}$$

where the last term $n_{\mathrm{H_2O(total)}} \log \mathrm{RH}$ is a fixed quantity for a known relative humidity, so can be ignored. The chemical equilibrium problem gives

$$\begin{aligned} \min \quad & G(n_l, \bar{n}_g, n_s, n_{\mathrm{H_2O(pm)}}) = n_c^T \log a_c + n_n^T(\log a_n + \log k_n) && \text{(22a)} \\ & + \bar{n}_g^T(\log \bar{a}_g + \log \bar{k}_g) + n_s^T \log k_s - n_{\mathrm{H_2O(pm)}} \log \mathrm{RH}, && \text{(22b)} \\ \text{s. t.} \quad & n_l = \begin{pmatrix} n_c \\ n_n \end{pmatrix} > 0, \quad n_g > 0, \quad n_s \geq 0, \quad n_{\mathrm{H_2O(pm)}} > 0 && \text{(22c)} \\ & n_c + A_n n_n + \bar{A}_g \bar{n}_g - n_{\mathrm{H_2O(pm)}} a_{\mathrm{H_2O}} + A_s n_s = \bar{b}. && \text{(22d)} \end{aligned}$$

The KKT system for the chemical equilibrium problem (22) can be written in the primal-dual canonical stoichiometric form:

$$\log a_c + \lambda = 0, \tag{23}$$
$$\log a_n + A_n^T \lambda = -\log k_n, \tag{24}$$
$$\log \bar{a}_g + \bar{A}_g^T \lambda = -\log \bar{k}_g, \tag{25}$$
$$\log \mathrm{RH} + a_{\mathrm{H_2O}}^T \lambda = 0, \tag{26}$$
$$\log k_s + A_s^T \lambda \geq 0, \quad n_s \geq 0, \tag{27}$$
$$n_s^T (\log k_s + A_s^T \lambda) = 0, \tag{28}$$
$$n_c + A_n n_n + \bar{A}_g \bar{n}_g - n_{\mathrm{H_2O(pm)}} a_{\mathrm{H_2O}} + A_s n_s = \bar{b}. \tag{29}$$

Remark 3.4. In atmospheric aerosol models such as SEQUILIB, SCAPE2, EQUISOLV II, and ISORROPIA, the amount of the water partitioned in the particle phase is assumed to be equal to the aqueous water content $n_{l,w}$, *i.e.* $n_{\mathrm{H_2O(pm)}} = n_{l,w}$, by neglecting the part of $n_{\mathrm{H_2O(pm)}}$ that is dissociated into electrolytes via

$$\mathrm{H_2O(aq)} \rightleftharpoons 2\mathrm{H}^+ + \mathrm{OH}^-.$$

The aqueous water content $n_{l,w}$ is usually predicted using an empirical relationship (Zdanovskii, Robinson and Stokes equation, ZSR (Ref. 23)). The shortcomings of this empirical method are the additional needs of the saturated molarities of electrolytes according to the relative humidity and, as a result, the thermodynamic inconsistency with the specific activity coefficient model that is used for the prediction of the activity of the aqueous phase.

From now on, let us drop the bar in the variables relative to the gas phase and replace $\bar{n}_g$ by n_g, etc.

In the KKT system of the primal-dual canonical stoichiometric form (23)-(29), the primal variables $n_{\mathrm{H_2O(pm)}}$ and n_s occur only in the mass balance constraints (29). They can be viewed respectively as the multipliers of the saturation constraints (26) and (27) on the dual variable λ, thus will be eliminated by applying the so-called null-space method for the solution of (23)-(29). This observation is the key for the development of the primal-dual active set algorithm detailed in the next section.

4 Active Set/Newton Method

4.1 Phase Stability Criterion and Active Set

A primal-dual solution of the KKT system (14)-(19) or (23)-(29), generally non-unique, is called a KKT point. But this solution may not be a local minimizer of the Gibbs free energy. One needs to perform a *phase stability analysis* to determine whether a postulated KKT point is thermodynamically stable with respect to any perturbation in n_l, n_g and n_s. Let $(n_l^\dagger, n_g^\dagger, n_s^\dagger, \lambda^\dagger)$ correspond to a KKT point of (14)-(19) or (23)-(29) and

$$\bar{\mathcal{I}}_s^\dagger := \{i \in \mathcal{I}_s : n_{s,i}^\dagger > 0\}, \tag{30}$$

and $\bar{m}_s := |\bar{\mathcal{I}}_s^\dagger|$. It is important to note that $\bar{\mathcal{I}}_s^\dagger$ is *a priori unknown*. In order to perform the phase stability analysis, the following *second order sufficient condition* is assumed. It states that,

$$p^T H p > 0, \quad \text{for all nonzero vector } p \text{ such that } \bar{A}p = 0. \tag{31}$$

In (31), $H = \nabla^2_{n_l,n_g,n_s} G(n_l^\dagger, n_g^\dagger, n_s^\dagger)$ is the Hessian matrix of the Gibbs free energy of the system, $\bar{A} = [A_l, A_g, \bar{A}_s]$ and $\bar{A}_s := (a_i^s)_{i\in\bar{\mathcal{I}}_s^\dagger}$. The following assumptions are also made:

(H1) The formula matrix $\bar{A}_s \in \mathbb{R}^{m_c \times \bar{m}_s}$ is assumed to be of full column rank with $\bar{m}_s \leq m_c$. This assumption is consistent with the chemical relation called *Gibbs phase rule*, see for instance (Ref. 24), giving an *a priori* estimate for the number of phases existing at the equilibrium. The full rank assumption implies the feasibility for the dual solution $\lambda^\dagger$ with respect to the saturation constraints

$$\log \bar{k}_s + \bar{A}_s^T \lambda^\dagger = 0, \quad \text{with } \bar{k}_s = (k_{s,i})_{i\in\bar{\mathcal{I}}_s^\dagger},$$

extracted from the complementary slackness conditions (18) or (28).

(H2) The formula vectors of solids actually precipitated in the system $(a_i^s)_{i\in\bar{\mathcal{I}}_s^\dagger}$ are assumed to be linearly independent (*linear independent constraints qualification*, see also (Ref. 25) for instance).

(H3) The strict complementary condition holds, *i.e.* $\log k_s + A_s^T\lambda \geq 0$, $n_s \geq 0$, $n_s^T(\log k_s + A_s^T\lambda) = 0$ (equivalent to (27) (28)), but also $n_s + (\log k_s + A_s^T\lambda) > 0$ (*i.e.* n_s and $(\log k_s + A_s^T\lambda)$ are not simultaneously zero).

Recall that the inertia of a symmetric matrix is an ordered set of three integers (i_+, i_-, i_o), where i_+ is the number of positive eigenvalues, i_- the number of negative eigenvalues, and i_0 the number of zero eigenvalues. For a generic matrix $A \in \mathbb{R}^{m\times n}$, let $Z_A \in \mathbb{R}^{n\times(n-m)}$ denote a null space matrix of A (*i.e.* a matrix such that $AZ_A = 0$). The relationship (31) is also equivalent to requiring the so-called KKT matrix

$$K = \begin{pmatrix} H & \bar{A}^T \\ \bar{A} & 0 \end{pmatrix},$$

to have a certain inertia. This is the subject of the next theorem.

Theorem 4.1. Under assumptions (H1) and (H2) and if (31) is satisfied, the KKT matrix K is invertible.

Proof. Based on an inertia result of Gould (Ref. 26), we have

$$\text{inertia}(K) = \text{inertia}(Z_{\bar{A}}^T H Z_{\bar{A}}) + (m_c, m_c, 0), \tag{32}$$

where $Z_{\bar{A}}$ is a null-space matrix for $\bar{A}$. Then (31) implies

$$\text{inertia}(K) = (m_l + m_g + \bar{m}_s, m_c, 0). \tag{33}$$

The matrix K is thus invertible. □

The difficulty in solving (14)-(19) or (23)-(29) is mainly caused by the combinatorial aspect of the KKT system, or more precisely by the complementary slackness conditions (18) or (28). The problem is not only to determine the concentrations but also to guess the *optimal active set* of solids (in the "dual" sense)

$$\bar{\mathcal{I}}_s^\dagger := \{\, j \in \mathcal{I}_s : \log k_{s,j} + a_{s,j}^T \lambda^\dagger = 0 \,\}. \tag{34}$$

Under assumption (H3) that the *strictly complementary slackness* condition holds, $\bar{\mathcal{I}}_s^\dagger$ is equal to the "primal" set defined in (30), *i.e.*, $\bar{\mathcal{I}}_s^\dagger := \{i \in \mathcal{I}_s : n_{s,i}^\dagger > 0\}$, the set of solid salts actually precipitated at equilibrium and the complementary solid set of $\bar{\mathcal{I}}_s^\dagger$

$$\tilde{\mathcal{I}}_s^\dagger := \mathcal{I}_s \setminus \bar{\mathcal{I}}_s^\dagger = \{\, j \in \mathcal{I}_s : \log k_{s,j} + a_{s,j}^T \lambda^\dagger > 0 \,\} \tag{35}$$

identifies the set of salts that are *subsaturated* with the aqueous solution. Under assumption (H3) again, the set $\tilde{\mathcal{I}}_s^\dagger$ is equal to $\tilde{\mathcal{I}}_s^\dagger = \{i \in \mathcal{I}_s : n_{s,i}^\dagger = 0\}$, the set of possible solid salts that are not precipitated at equilibrium.

Based on a guess of the optimal active set of solid phases (34), the KKT system (14)-(19) or (23)-(29) can be transformed into a system of nonlinear equations, which is much more computationally tractable. With the notations

$$\bar{A}_s := (a_j^s)_{j\in\bar{\mathcal{I}}_s^\dagger}, \quad \tilde{A}_s := (a_j^s)_{j\in\tilde{\mathcal{I}}_s^\dagger}, \quad \bar{n}_s := (n_{s,j})_{j\in\bar{\mathcal{I}}_s^\dagger}, \quad \text{and } \tilde{n}_s := (n_{s,j})_{j\in\tilde{\mathcal{I}}_s^\dagger},$$

the *exact solution* of the chemical equilibrium problem (22) can be computed from the following KKT system of equations:

$$\log a_c + \lambda = 0, \tag{36}$$
$$\log a_n + A_n^T\lambda = -\log k_n, \tag{37}$$
$$\log a_g + A_g^T\lambda = -\log k_g, \tag{38}$$
$$\log \mathrm{RH} + a_{\mathrm{H_2O}}^T\lambda = 0, \tag{39}$$
$$\log \bar{k}_s + \bar{A}_s^T\lambda = 0, \quad \bar{n}_s > 0, \tag{40}$$
$$\log \tilde{k}_s + \tilde{A}_s^T\lambda > 0, \quad \tilde{n}_s = 0, \tag{41}$$
$$n_c + A_n n_n + A_g n_g - n_{\mathrm{H_2O(pm)}} a_{\mathrm{H_2O}} + \bar{A}_s\bar{n}_s = \bar{b}, \tag{42}$$

where the complementary slackness conditions (27) and (28) are split into the equalities (40) and the strict inequalities (41), according to the optimal active and inactive sets of solid phases, $\bar{\mathcal{I}}_s^\dagger$ and $\tilde{\mathcal{I}}_s^\dagger$, respectively.

In order to simplify the notations, let

$$\bar{A}_\lambda = (-a_{\mathrm{H_2O}}, \bar{A}_s)^T, \quad \bar{m}_\lambda = \bar{m}_s + 1, \quad \text{and } \bar{b}_\lambda = (\log \mathrm{RH}, -\log \bar{k}_s^T)^T.$$

The "dual" saturation constraints (39) and (40) are combined to form the dual linear equality constraint

$$\bar{A}_\lambda\lambda = \bar{b}_\lambda. \tag{43}$$

The feasibility of (43) requires $\bar{A}_\lambda$ to be of full row rank, implying that $\bar{A}_s$ *must be of full column rank and that* $a_{H_2O} \notin$ *range*$(\bar{A}_s)$. Notice that the latter is always true if the solid salts do not contain hydrated water.

The dual variable λ that satisfies (43) can be expressed in terms of a reduced variable η via

$$\lambda = \lambda^* + Z_{\bar{A}_\lambda}\eta,$$

where $Z_{\bar{A}_\lambda}$ is a null-space matrix of $\bar{A}_\lambda$ and λ^* is a particular solution of (43). The primal variables $n_{\mathrm{H_2O(pm)}}$ and $\bar{n}_s$ are viewed as the multiplier of the combined dual equality constraint (43). Replacing λ by the reduced variable η and projecting the KKT system (36)-(42) onto the null-space $Z_{\bar{A}_\lambda}$ to eliminate $(n_{\mathrm{H_2O(pm)}}, \bar{n}_s)$, gives the following *reduced KKT system of the primal-dual canonical stoichiometric equations*:

$$\log a_c + Z_{\bar{A}_\lambda}\eta = -\lambda^*, \tag{44}$$
$$\log a_n + A_n^T Z_{\bar{A}_\lambda}\eta = -\log k_n - A_n^T\lambda^*, \tag{45}$$
$$\log a_g + A_g^T Z_{\bar{A}_\lambda}\eta = -\log k_g - A_g^T\lambda^*, \tag{46}$$
$$Z_{\bar{A}_\lambda}^T n_c + Z_{\bar{A}_\lambda}^T A_n n_n + Z_{\bar{A}_\lambda}^T A_g n_g = Z_{\bar{A}_\lambda}^T \bar{b}. \tag{47}$$

Once the solution (n_c, n_n, n_g, η) of the reduced system (44)-(47) is known, one can compute the primal variables $n_{\mathrm{H_2O(pm)}} > 0$ and $\bar{n}_s > 0$, from the mass-balance equations (42) via

$$\begin{pmatrix} n_{\mathrm{H_2O(pm)}} \\ \bar{n}_s \end{pmatrix} = \left(\bar{A}_\lambda^T\right)^{-1}\left(\bar{b} - n_c - A_n n_n - A_g n_g\right) \tag{48}$$

where $\left(\bar{A}_\lambda^T\right)^{-1}$ is the left pseudoinverse of $\bar{A}_\lambda^T$. From now on, let us denote by $\bar{n}_s$ the union of $\bar{n}_s$ and $n_{\mathrm{H_2O(pm)}}$. Note that the set of all possible active sets grows exponentially with m_s, the number of all possible solid salts considered.

4.2 Primal-Dual Active Set Method

In order to solve (14)-(19) or (23)-(29), a primal-dual algorithm is presented, based on the active-set strategy that makes a sequence of sets converging to the optimal active set of solid phases. This sequence of the so-called active sets, denoted by $\bar{\mathcal{I}}_s$, is defined in the "dual" sense as it was done for the optimal active set $\bar{\mathcal{I}}_s^\dagger$ in (34) by

$$\bar{\mathcal{I}}_s := \{\, j \in \mathcal{I}_s : \log k_{s,j} + a_{s,j}^T\lambda = 0 \,\}, \tag{49}$$

where the dual variable λ, together with the primal variable (n_l, n_g, n_s) consists of a sequence of iterates that converges to the primal-dual solution

$(n_l^\dagger, n_g^\dagger, n_s^\dagger, \lambda^\dagger)$ of the KKT system (23)-(29). By the definition (49), $\bar{\mathcal{I}}_s$ is the set of the linear inequalities (27) becoming active at λ. Starting as an approximation of $\bar{\mathcal{I}}_s^\dagger$, *a priori* unknown, the set $\bar{\mathcal{I}}_s$ is expected to converge quickly to the optimal active set $\bar{\mathcal{I}}_s^\dagger$ as soon as λ is in a neighborhood of $\lambda^\dagger$. The complementary solid set of $\bar{\mathcal{I}}_s$, denoted by $\tilde{\mathcal{I}}_s$, is the set of the linear inequalities (27) being inactive at λ, *i.e.*,

$$\tilde{\mathcal{I}}_s := \mathcal{I}_s \setminus \bar{\mathcal{I}}_s = \{\, j \in \mathcal{I}_s : \log k_{s,j} + a_{s,j}^T \lambda > 0 \,\}. \tag{50}$$

In our active-set algorithm, the sequence of the dual variable λ is required to satisfy the active constraints in $\bar{\mathcal{I}}_s$ as equalities, *i.e.*,

$$\log k_{s,j} + a_{s,j}^T \lambda = 0, \quad \forall j \in \bar{\mathcal{I}}_s, \tag{51}$$

and stay feasible with respect to the inequality constraints that are inactive, *i.e.*,

$$\log k_{s,j} + a_{s,j}^T \lambda \geq 0, \quad \forall j \in \tilde{\mathcal{I}}_s. \tag{52}$$

The principle of the algorithm is the following. The dual feasibility condition of inequalities (52) enforces the dual variables to remain feasible with respect to the inequality constraints, until the *saturation* is reached at an iteration and the inequality constraint is set to be *active* and is added into the active set. The dual feasibility condition of equalities (51) enforces every active constraint to remain active, until the corresponding primal variable $n_{s,j}$ becomes *negative* at a certain iteration and the corresponding equality constraint is set to be *inactive* and becomes an inequality. Thus the corresponding salt is removed from the active set.

The problem is to construct a sequence of active sets which converges to $\bar{\mathcal{I}}_s^\dagger$. The active set strategy is the following. Along the process of applying the active-set strategy, the KKT system (23)-(29) is first projected onto the current active set $\bar{\mathcal{I}}_s$ to form a reduced KKT system of the form similar to that of (44)-(47) with the particular solution λ^* of (43) being the current dual variable λ.

Then one Newton iteration is applied to the reduced system to find the next *primal-dual* approximation (n_l, n_g, λ) of the solution, where the new estimate of λ is updated from the current one by stepping along a null-space direction defined by $Z_{\bar{A}_\lambda}$. The displacement along this direction is restricted to a certain length so that λ stays feasible with respect to (52).

Finally, the next active set $\bar{\mathcal{I}}_s$ is obtained by adding constraints that are encountered by the new λ and the KKT system (23)-(29) is projected onto the new active set. Once the sequence of (n_l, n_g, λ) has converged to a solution of the reduced KKT system, the concentrations $\bar{n}_s$ of the *saturated salts* in the active set are computed via equation (48). Since $\bar{n}_s$ is viewed as the Lagrange *multipliers* of the dual active constraints (51), its non-negativeness is enforced by *removing a saturated salt* from the active set $\bar{\mathcal{I}}_s$ when its concentration becomes *negative*. The above process continues until the equilibrium set of solid phases $\bar{\mathcal{I}}_s^\dagger$ is obtained.

Let us ignore (for the moment) the fact that $\bar{n}_s$ must remain non-negative, and simply apply Newton's method to the reduced KKT system projected on $\bar{\mathcal{I}}_s$ to compute a displacement in (n_l, n_g, λ) denoted by $(p_{n_l}, p_{n_g}, p_\lambda)$ with $p_\lambda = Z_{\bar{A}_\lambda} p_{\boldsymbol{\eta}}$ for a certain $\boldsymbol{\eta}$ as λ must satisfy (51). The reduced KKT system is the following symmetric indefinite system:

$$\begin{pmatrix} H_l & 0 & A_{zl}^T \\ 0 & H_g & A_{zg}^T \\ A_{zl} & A_{zg} & 0 \end{pmatrix} \begin{pmatrix} p_l \\ p_g \\ p_{\boldsymbol{\eta}} \end{pmatrix} = \begin{pmatrix} b_l \\ b_g \\ b_{\boldsymbol{\eta}} \end{pmatrix}, \tag{53}$$

where

$$\begin{aligned} &H_l = \nabla(\log a_l), \quad H_g = \nabla(\log a_g) = \text{ diag } (1/n_g), \\ &A_{zl} = Z_{\bar{A}_\lambda}^T A_l, \quad A_{zg} = Z_{\bar{A}_\lambda}^T A_g, \end{aligned}$$

and

$$\begin{aligned} b_l &= -\log k_l - \log a_l - A_l^T \lambda, \\ b_g &= -\log k_g - \log a_g - A_g^T \lambda, \\ b_{\boldsymbol{\eta}} &= Z_{\bar{A}_\lambda}^T \left(\bar{b} - A_l n_l - A_g n_g \right). \end{aligned}$$

Note that A_{zl} is of full rank. Let

$$\tilde{\mathcal{I}}_g := \{ j \in \mathcal{I}_g : \ Z_{\bar{A}_\lambda}^T a_j^g = 0 \}, \tag{54}$$

$$\bar{\mathcal{I}}_g := \mathcal{I}_g \setminus \tilde{\mathcal{I}}_g, \quad \bar{m}_g := |\bar{\mathcal{I}}_g|, \tag{55}$$

$$\bar{A}_g := (a_j^g)_{j \in \bar{\mathcal{I}}_g}, \quad \bar{A}_{zg} := Z_{\bar{A}_\lambda}^T \bar{A}_g. \tag{56}$$

Note that $\bar{A}_{zg}$ is of full rank and we have then

$$A_{zg} P = (\bar{A}_{zg}, 0), \tag{57}$$

where P is a permutation matrix.

The displacement in λ is obtained from p_η as a displacement in the null-space, defined by $p_\lambda = Z_{\bar{A}_\lambda} p_\eta$. A new estimate of the solution of the KKT system (23)-(29) is then obtained by

$$
\begin{aligned}
n_l^+ &= n_l + \alpha\, p_l, && (58a)\\
n_g^+ &= n_g + \alpha\, p_g, && (58b)\\
\lambda^+ &= \lambda + \alpha\, p_\lambda. && (58c)
\end{aligned}
$$

The parameter α is a steplength computed by

$$\alpha = \min(\bar{\alpha}, \alpha_{\max}),$$

where $\alpha_{\max}$ is a fixed upper bound on the steplength and $\bar{\alpha}$ is the maximum *feasible steplength* that can be taken along the direction p_λ. The parameter $\alpha_{\max}$ is usually taken to be 1; it can also be adjusted to ensure that a *merit function* is sufficiently reduced so that the primal-dual method converges globally, see *e.g.* (Ref. 27). The maximum feasible steplength $\bar{\alpha}$ is computed by using a ratio test

$$\bar{\alpha} \;=\; \min \left\{ \frac{\log k_{s,j} + a_{s,j}^T \lambda}{-a_{s,j}^T p_\lambda} \;:\; a_{s,j}^T p_\lambda < 0,\; j \notin \bar{\mathcal{I}}_s \right\}, \qquad (59)$$

so that the new estimate λ^+ stays feasible with respect to the inequality constraints (52), *i.e.* $\log \tilde{k}_s + \tilde{A}_s^T \lambda^+ \geq 0$. A step α is called *restricted* if $\alpha < \alpha_{\max}$, i.e, a constraint is encountered by λ^+ in the line-search. Otherwise, the step is referred to as *unrestricted*. As λ^+ is updated along a null-space direction, it satisfies naturally (51).

The updates of the active sets are now described, starting with the addition of constraints into the active set. The initial active-set $\bar{\mathcal{I}}_s^0$ is required to only contain constraints that are active at λ^0. By the feasibility arguments (43), the associated matrix $\bar{A}_s^0$ is of full rank, so is $\bar{A}_\lambda^0$. Let $\mathcal{P}^a$ denote the index set of constraints that are encountered by λ^+ in the line-search at a Newton iteration, *i.e.*,

$$\mathcal{P}^a = \{\, j \notin \bar{\mathcal{I}}_s : \, a_{s,j}^T p_\lambda < 0,\, \log k_{s,j} + a_{s,j}^T \lambda^+ = 0 \,\}.$$

Note that $\mathcal{P}^a$ may be the empty set. The new active set is then defined by

$$\bar{\mathcal{I}}_s^+ = \bar{\mathcal{I}}_s \cup \bar{\mathcal{I}}_s^a,$$

where $\bar{\mathcal{I}}_s^a \subseteq \mathcal{P}^a$ is required to satisfy

$$\mathcal{P}^a \neq \emptyset \quad \text{implies} \quad \bar{\mathcal{I}}_s^a \neq \emptyset. \tag{60}$$

The implication of (60) is that if new constraints are encountered in the line-search, at least one of them must be added, and also that no all the constraints encountered need to be active. In practice, exactly one new constraint is added at one time. Since λ^+ satisfies all the constraints in $\bar{\mathcal{I}}_s^+$, by the feasibility arguments (43), the associated matrix $\bar{A}_s^+$ must have full rank, so does $\bar{A}_\lambda^+$, see also (Ref. 28).

On the other hand, the choice of a rule for removing constraints from the active-set is now detailed. As described before, the solution (n_l, n_g, λ) is computed by Newton's method and the constraints encountered by λ in the line-search are added to the active set $\bar{\mathcal{I}}_s$, until the sequence of Newton iterates (n_l, n_g, λ) converges to a solution of the reduced KKT system (44)-(47) which satisfies the inequality constraints. The concentrations $\bar{n}_s$ are then computed and the set

$$\mathcal{P}^d = \{\, j \in \bar{\mathcal{I}}_s : \, n_{s,j} < 0 \,\}$$

is identified. If $\mathcal{P}^d \neq \emptyset$, the new active set is defined by

$$\bar{\mathcal{I}}_s^+ = \bar{\mathcal{I}}_s \setminus \bar{\mathcal{I}}_s^d,$$

where $\bar{\mathcal{I}}_s^d \subseteq \mathcal{P}^d$ is required to satisfy

$$\mathcal{P}^d \neq \emptyset \quad \text{implies} \quad \bar{\mathcal{I}}_s^d \neq \emptyset. \tag{61}$$

The implication of (61) is that if solid salts have negative concentrations, at least one of them must be removed, and also that no all the solid salts having negative concentrations need to be inactive. In practice, only one constraint is removed at one time. The KKT system is then projected on the new active set and a new loop of Newton iterations is restarted until convergence is achieved.

If $\mathcal{P}^d = \emptyset$, a feasible solution of (23)-(29) is reached, and the algorithm stops. This active set/Newton algorithm is summarized in Table 1.

Table 1. Active set/Newton method: summary of the algorithm.

Step 0. Initial n_l^0, n_g^0, λ^0 and $\bar{\mathcal{I}}_s$ are given;

Step 1. Compute the reduced Newton direction (p_l, p_g, p_λ) by solving (53);

Step 2. Compute the steplength $\bar{\alpha}$ with (59);

Step 3. Update n_l^+, n_g^+ and $\boldsymbol{\lambda}^+$ with (58);

Step 4. Test if the Newton method converged;

(a) If no, consider the steplength $\bar{\alpha}$:

- if $\bar{\alpha} < 1$ (restricted step), update $\bar{\mathcal{I}}_s^+ = \bar{\mathcal{I}}_s \cup \{i\}$ and go to (1);
- if $\bar{\alpha} \geq 1$ (unrestricted step), go to (1).

(b) If yes, compute the primal variables $\bar{n}_s^+$ and $n_{\mathrm{H_2O}}^+$ with (48):

- If $\bar{n}_s^+, n_{\mathrm{H_2O}}^+ \geq 0$, STOP;
- If $\exists j \in \{1, \ldots, n_s\}$ such that $\bar{n}_{s,j}^+ < 0$, update $\bar{\mathcal{I}}_s^+ = \bar{\mathcal{I}}_s \backslash \{j\}$ and go to (1)

Remark 4.1. In comparison with other thermodynamic models, this algorithm neither assumes $n_{\mathrm{H_2O(pm)}} = n_{l,w}$, nor uses the ZSR relationship in its prediction of the amount of the water partitioned in the particulate phase at a fixed relative humidity.

4.3 Computation of Newton Direction

Consider the linear KKT system (53) and define the associated KKT matrix

$$\bar{K} = \begin{pmatrix} H_l & 0 & A_{zl}^T \\ 0 & H_g & A_{zg}^T \\ A_{zl} & A_{zg} & 0 \end{pmatrix}.$$

First note that the Hessian matrix of the gas phase $H_g = \mathrm{diag}(1/n_g)$ is positive definite with inverse $H_g^{-1} = \mathrm{diag}(n_g)$.

Lemma 4.1. The condition (33) is equivalent to

$$\mathrm{inertia}(\bar{K}) = (m_l + m_g, m_{zc}, 0), \tag{62}$$

where $m_{zc} = m_c - \bar{m}_\lambda$.

Proof. The proof is a direct consequence of (32) applied to the matrix $\bar{K}$. □

Let $\bar{A}_{zg}$ and A_{zl}^T have the following QR factorizations:

$$\bar{A}_{zg} = (Q_g \ \tilde{Q}_g) \begin{pmatrix} R_g \\ 0 \end{pmatrix} = Q_g R_g, \quad A_{zl}^T = (Q_l \ \tilde{Q}_l) \begin{pmatrix} R_l \\ 0 \end{pmatrix} = Q_l R_l,$$

where $(Q_g \ \tilde{Q}_g)$ and $(Q_l \ \tilde{Q}_l)$ are orthogonal with $Q_g \in \mathbb{R}^{m_{zc} \times \bar{m}_g}$, $\tilde{Q}_g \in \mathbb{R}^{m_{zc} \times (m_{zc} - \bar{m}_g)}$, $Q_l \in \mathbb{R}^{m_l \times m_{zc}}$, and $\tilde{Q}_l \in \mathbb{R}^{m_l \times (m_l - m_{zc})}$, and $R_g \in \mathbb{R}^{\bar{m}_g \times \bar{m}_g}$ and $R_l \in \mathbb{R}^{m_{zc} \times m_{zc}}$ are nonsingular.

Theorem 4.2. The condition (31), together with the assumptions (H1) (H2), is equivalent to

$$Z_{A_{zl}}^T H_l Z_{A_{zl}} > 0, \tag{63}$$

$$\tilde{Z}_{A_{zl}}^T H_l \tilde{Z}_{A_{zl}} + R_g^{-T} \bar{H}_g R_g^{-1} > 0. \tag{64}$$

where $\tilde{Z}_{A_{zl}} = Q_l R_l^{-T} Q_g$ and $\bar{H}_g = \mathrm{diag}(1/n_j^g)_{j \in \bar{\mathcal{I}}_g}$. Conditions (63) and (64) are sufficient conditions for the system (53) to be solvable.

Proof. The following proof is a constructive proof that also emphasize the solution method of (53) and the computation of the Newton direction.

The range-space method is applied to eliminate p_g from (53), giving

$$\begin{pmatrix} H_l & A_{zl}^T \\ A_{zl} & -S_g \end{pmatrix} \begin{pmatrix} p_l \\ p_\eta \end{pmatrix} = \begin{pmatrix} b_l \\ c_\eta \end{pmatrix}, \tag{65}$$

where $c_\eta = b_\eta - A_{zg} H_g^{-1} b_g$ and $S_g = A_{zg} H_g^{-1} A_{zg}^T$ is the Schur complement. Once (65) is solved, p_g can be easily obtained from p_η via

$$p_g = H_g^{-1}(b_g - A_{zg}^T p_\eta). \tag{66}$$

Let

$$\tilde{K} = \begin{pmatrix} H_l & A_{zl}^T \\ A_{zl} & -S_g \end{pmatrix}.$$

Lemma 4.2. Relationship (62) is equivalent to

$$\text{inertia}(\tilde{K}) = (m_l, m_{zc}, 0). \tag{67}$$

Proof. The inertia relation, see for instance (Ref. 26), leads to

$$\text{inertia}(\bar{K}) = \text{inertia}(H_g) + \text{inertia}(\tilde{K}),$$

and the conclusion holds since $\text{inertia}(H_g) = (m_g, 0, 0)$. □

Let us turn to the solution of (65). It follows from (57) that

$$S_g = A_{zg} H_g^{-1} A_{zg}^T = A_{zg} P P^T H_g^{-1} P P^T A_{zg}^T = \bar{A}_{zg} \bar{H}_g^{-1} \bar{A}_{zg}^T.$$

Then, the inertia of S_g is given by

$$\text{inertia}(S_g) = \begin{cases} (\bar{m}_g, 0, m_{zc} - \bar{m}_g), & \text{if } m_{zc} \geq \bar{m}_g, \\ (m_{zc}, 0, 0), & \text{otherwise.} \end{cases} \tag{68}$$

The condition (68) implies that S_g is positive definite only if the number of saturated salts becomes larger than the number of components subtracted by the number of "active" gas species ($\bar{m}_s \geq m_c - \bar{m}_g$); otherwise, S_g is positive semi-definite. Note that H_l is singular, due to the Gibbs-Duhem relation (7).

For the solution of the system (65), the nullity of S_g has to be eliminated first. Consider the QR factorization of A_{zg}. Then it is easy to see that the Schur complement S_g has the block structure

$$S_g = (Q_g \ \tilde{Q}_g) \begin{pmatrix} R_g \bar{H}_g^{-1} R_g^T & 0 \\ 0 & 0 \end{pmatrix} \begin{pmatrix} Q_g^T \\ \tilde{Q}_g^T \end{pmatrix}.$$

Lemma 4.3. By defining $p_{\eta_1} = Q_g^T p_\eta$ and $p_{\eta_2} = \tilde{Q}_g^T p_\eta$, the linear system (65) is equivalent to solving

$$\begin{pmatrix} H_l + S_l & A_{zl}^T \tilde{Q}_g \\ \tilde{Q}_g^T A_{zl} & 0 \end{pmatrix} \begin{pmatrix} p_l \\ p_{\eta_2} \end{pmatrix} = \begin{pmatrix} c_l \\ \tilde{Q}_g^T c_\eta \end{pmatrix}, \tag{69}$$

where

$$c_l = b_l + A_{zl}^T Q_g R_g^{-T} \bar{H}_g R_g^{-1} Q_g^T c_\eta, \tag{70}$$

$$S_l = A_{zl}^T Q_g R_g^{-T} \bar{H}_g R_g^{-1} Q_g^T A_{zl}. \tag{71}$$

Proof. Let

$$V = \begin{pmatrix} I_{m_l} & 0 \\ 0 & Q \end{pmatrix}.$$

Hence

$$V^T \tilde{K} V = \begin{pmatrix} H_l & A_{zl}^T Q \\ Q^T A_{zl} & -Q^T S_g Q \end{pmatrix} = \begin{pmatrix} H_l & A_{zl}^T Q_g & A_{zl}^T \tilde{Q}_g \\ Q_g^T A_{zl} & -R_g \bar{H}_g^{-1} R_g^T & 0 \\ \tilde{Q}_g^T A_{zl} & 0 & 0 \end{pmatrix}. \tag{72}$$

The system (65) is multiplied by V^T from the left on both sides and (72) is used to write the resulting system as a 3×3 block system. With symmetrically block rows and columns permutations, the resulting linear system is:

$$\begin{pmatrix} -R_g \bar{H}_g^{-1} R_g^T & Q_g^T A_{zl} & 0 \\ A_{zl}^T Q_g & H_l & A_{zl}^T \tilde{Q}_g \\ 0 & \tilde{Q}_g^T A_{zl} & 0 \end{pmatrix} \begin{pmatrix} p_{\eta_1} \\ p_l \\ p_{\eta_2} \end{pmatrix} = \begin{pmatrix} Q_g^T c_\eta \\ b_l \\ \tilde{Q}_g^T c_\eta \end{pmatrix}. \tag{73}$$

Since $-R_g \bar{H}_g^{-1} R_g^T$, the $(1,1)$ block, is nonsingular, the range-space method is applied to eliminate p_{η_1} from (73), giving (69) - (71). □

Note that, with the definitions in Lemma 4.3, p_η is obtained from

$$p_\eta = (Q_g \;\; \tilde{Q}_g) \begin{pmatrix} p_{\eta_1} \\ p_{\eta_2} \end{pmatrix} = Q_g p_{\eta_1} + \tilde{Q}_g p_{\eta_2}. \tag{74}$$

Once (69) is solved, the direction p_{η_1} can easily be obtained from p_l via

$$p_{\eta_1} = -R_g^{-T} \bar{H}_g R_g^{-1} Q_g^T (c_\eta - A_{zl} p_l). \tag{75}$$

Then let us define the matrix $\ddot{K}$ of the linear system (69) by

$$\ddot{K} = \begin{pmatrix} H_l + S_l & A_{zl}^T \tilde{Q}_g \\ \tilde{Q}_g^T A_{zl} & 0 \end{pmatrix}. \tag{76}$$

A stability analysis for the solvability of the system (69) is performed in the next lemma.

Lemma 4.4. The condition (67) is equivalent to the condition

$$Z_l^T (H_l + S_l) Z_l > 0, \tag{77}$$

where $Z_l \in \mathbb{R}^{m_l \times (m_l - m_{zc} + \bar{m}_g)}$ is a null-space matrix of $\tilde{Q}_g^T A_{zl}$. Under condition (62) or (77), the linear system (69) is solvable.

Proof. Relationship (32) leads to

$$\text{inertia}(\tilde{K}) = \text{inertia}(-R_g \bar{H}_g^{-1} R_g^T) + \text{inertia}(\ddot{K}).$$

Since $R_g \bar{H}_g^{-1} R_g^T > 0$, relationship (67) implies that

$$\text{inertia}(\ddot{K}) = (m_l, m_{zc} - \bar{m}_g, 0). \tag{78}$$

The Schur complement S_l in (76) is positive semidefinite. Since $\tilde{Q}_g^T A_{zl} \in \mathbb{R}^{(m_{zc} - \bar{m}_g) \times m_l}$ in (76) is of full rank $m_{zc} - \bar{m}_g$ by (32), we have

$$\text{inertia}(\ddot{K}) = \text{inertia}(Z_l^T (H_l + S_l) Z_l) + (m_{zc} - \bar{m}_g, m_{zc} - \bar{m}_g, 0),$$

Relationship (78) implies that

$$\text{inertia}(Z_l^T (H_l + S_l) Z_l) = (m_l - m_{zc} + \bar{m}_g, 0, 0)$$

which is equivalent to (77) and the desired conclusion follows □

A particular matrix Z_l is now considered. To construct Z_l, let us consider the QR factorization of A_{zl}^T. Then, we have

$$A_{zl} = R_l^T Q_l^T, \quad A_{zl}^{-1} = Q_l R_l^{-T},$$

where A_{zl}^{-1} is the right pseudoinverse of A_{zl}, *i.e.* $A_{zl}A_{zl}^{-1} = I_{m_{zc}}$. The matrix Z_l is defined as the following null-space matrix of $\tilde{Q}_g^T A_{zl}$:

$$Z_l = (Z_{A_{zl}}, \tilde{Z}_{A_{zl}}),$$

where

$$Z_{A_{zl}} = \tilde{Q}_l, \quad \tilde{Z}_{A_{zl}} = A_{zl}^{-1} Q_g = Q_l R_l^{-T} Q_g.$$

Note that

$$Z_l^T Z_l = \begin{pmatrix} \tilde{Q}_l^T \\ Q_g^T R_l^{-1} Q_l^T \end{pmatrix} (\tilde{Q}_l \;\; Q_l R_l^{-T} Q_g) = \begin{pmatrix} I_{m_l - m_{zc}} & 0 \\ 0 & Q_g^T R_l^{-1} R_l^{-T} Q_g \end{pmatrix}.$$

From the condition (77), we have

$$\begin{aligned} 0 < Z_{A_{zl}}^T (H_l + S_l) Z_{A_{zl}} &= Z_{A_{zl}}^T H_l Z_{A_{zl}} + Z_{A_{zl}}^T S_l Z_{A_{zl}}, \\ 0 < \tilde{Z}_{A_{zl}}^T (H_l + S_l) \tilde{Z}_{A_{zl}} &= \tilde{Z}_{A_{zl}}^T H_l \tilde{Z}_{A_{zl}} + \tilde{Z}_{A_{zl}}^T S_l \tilde{Z}_{A_{zl}}. \end{aligned}$$

Taking into account of the definition of S_l in (71), we have

$$\begin{aligned} Z_{A_{zl}}^T S_l Z_{A_{zl}} &= Z_{A_{zl}}^T A_{zl}^T Q_g R_g^{-T} \bar{H}_g R_g^{-1} Q_g^T A_{zl} Z_{A_{zl}} = 0, \\ \tilde{Z}_{A_{zl}}^T S_l \tilde{Z}_{A_{zl}} &= Q_g^T A_{zl}^{-T} A_{zl}^T Q_g R_g^{-T} \bar{H}_g R_g^{-1} Q_g^T A_{zl} A_{zl}^{-1} Q_g \\ &= R_g^{-T} \bar{H}_g R_g^{-1} > 0. \end{aligned}$$

Thus, (77) is equivalent to require that the conditions (63) and (64) hold and the conclusion of the theorem holds. □

Remark 4.2. Note that the condition (63), *i.e.*, $Z_{A_{zl}}^T H_l Z_{A_{zl}} > 0$, implies that

$$\text{inertia} \begin{pmatrix} H_l & A_{zl}^T \\ A_{zl} & 0 \end{pmatrix} = (m_l, m_{zc}, 0).$$

That is, if $\bar{m}_g = 0$, the condition (63) alone implies that K has the desire inertia (33). For $\bar{m}_g > 0$, the additional condition (64) is required.

From the solvability condition (77) that is derived from the above analysis on the phase stability, the system (69) is then solved by the null-space method. To ensure that the primal-dual algorithm converges to a minimum or stable equilibrium rather than any other first order optimality point such as a maximum or a saddle point, the condition (31) is enforced by controlling H_l at each iteration, *i.e.* by replacing H_l by a modification $\tilde{H}_l$ if $Z_l^T(H_l+S_l)Z_l$ is not sufficiently positive definite so that $Z_l^T(\tilde{H}_l+S_l)Z_l$ is sufficiently positive definite. Various methods for modifying H_l may be found in (Ref. 29) for instance. Note that

$$Z_l^T(\tilde{H}_l+S_l)Z_l = Z_l^T\tilde{H}_lZ_l + \begin{pmatrix} 0 & 0 \\ 0 & R_g^{-T}\bar{H}_gR_g^{-1} \end{pmatrix}.$$

The system (69) or, more precisely, the system

$$\begin{pmatrix} \tilde{H}_l+S_l & A_{zl}^T\tilde{Q}_g \\ \tilde{Q}_g^TA_{zl} & 0 \end{pmatrix} \begin{pmatrix} p_l \\ p_{\eta_2} \end{pmatrix} = \begin{pmatrix} c_l \\ \tilde{Q}_g^Tc_\eta \end{pmatrix} \tag{79}$$

has the solution given by:

$$p_l = Z_l(Z_l^T(\tilde{H}_l+S_l)Z_l)^{-1}Z_l^T\left(c_l-(\tilde{H}_l+S_l)p_l^*\right)+p_l^*, \tag{80}$$

$$p_{\eta_2} = \left(A_{zl}^T\tilde{Q}_g\right)^{-1}\left(c_l-(\tilde{H}_l+S_l)p_l\right), \tag{81}$$

where $\left(A_{zl}^T\tilde{Q}_g\right)^{-1}$ is the left pseudoinverse of $A_{zl}^T\tilde{Q}_g$, given by

$$\left(A_{zl}^T\tilde{Q}_g\right)^{-1} = \tilde{Q}_g^T(A_{zl}^{-1})^T,$$

and p_l^* is a particular solution of the second equation of (79), given by

$$p_l^* = A_{zl}^{-1}c_\eta.$$

In summary, for the solution of (53), the combination of Schur complements and null-space methods permits to solve successively (79) to obtain p_l and $p_{\boldsymbol{\eta}_2}$. Then p_{η_1} is obtained from (75), giving p_η with (74) and $p_\lambda = Z_{\bar{A}_\lambda}p_\eta$. Finally p_g is obtained with (66) to increment all the variables (n_l, n_g, λ) for next iteration.

5 Numerical Results

The primal-dual active set algorithm has been implemented into UHAERO, a general thermodynamic model that can predict efficiently and accurately the phase transition and multistage growth phenomena of inorganic aerosols under a wide range of atmospheric conditions. Physical parameters as temperature, relative humidity and pressure are input parameters, as well as the feed vector $\bar{b}$ and stoichiometry matrix $A = [A_l, A_g, A_s]$. The Gibbs free energy and the activity coefficients are computed with the *Extended UNIQUAC* model, see for instance (Ref. 30). Two numerical examples in the multi-stage growth of atmospheric aerosols are considered here to illustrate the efficiency of the algorithm.

5.1 Sulfate Aerosols

A sulfate aerosol $(NH_4)_2SO_4$-H_2SO_4-H_2O is assumed to be diluted in the air. Three solid phases (A:$(NH_4)_2SO_4$, B:$(NH_4)_3H(SO_4)_2$ and C:NH_4HSO_4) may possibly appear at equilibrium. The chemical reactions which may appear between the chemical components of the system are given in Table 2.

The vapor-liquid equilibrium reaction expresses the changes between water (l/aq = liquid/aqueous phase) and water vapor (g=gas phase), in which the relative humidity is a given constant; the speciation equilibria describe the interactions in the aqueous phase, while the solid-liquid equilibria are the reactions giving birth to a solid phase. In Figure 1, the reconstructed sulfate aerosol phase diagram is illustrated. For each weight ratio of the feed vector $\bar{b}$, the method allows to predict the existence or non-existence of each solid phase and the weight amount of water in the aerosol particle due to the instantaneous vapor-liquid equilibrium. The level lines of the relative humidity show easily that, for high relative humidity, no solid salts appear at equilibrium. In Figure 2, the evolution of the aerosol particle with the feed vector $\bar{b}$ corresponding to three solids A, B and C in Figure 1, respectively, are illustrated in function of the *relative humidity* RH. For each feed ratios of the aerosol particle, the figure shows that the phase changes are very accurately tracked by discontinuities in the trajectory. Figure 3 shows the typical Newton iteration in UHAERO.

Table 2. Chemical equilibrium reactions in the sulfate aerosol. The first class denotes the vapor-liquid equilibrium; the second class describes the reactions in the aqueous phase, without phase changes; finally the third class is the reactions with phase changes which may lead to the creation of a solid.

- Vapor-Liquid Equilibrium:

  $H_2O(l) \rightleftarrows H_2O(g)$
  $NH_3(l) \rightleftarrows NH_3(g)$
  $H_2SO_4(l) \rightleftarrows H_2SO_4(g)$

- Speciation Equilibria:

  $H_2SO_4(l) \rightleftarrows H^+(aq) + HSO_4^-(aq)$
  $HSO_4^-(aq) \rightleftarrows H^+(aq) + SO_4^{2-}(aq)$
  $NH_3(l) + H_2O(l) \rightleftarrows NH_4^+(aq) + OH^-(aq)$
  $H_2O(l) \rightleftarrows H^+(aq) + OH^-(aq)$

- Solid-Liquid Equilibria:

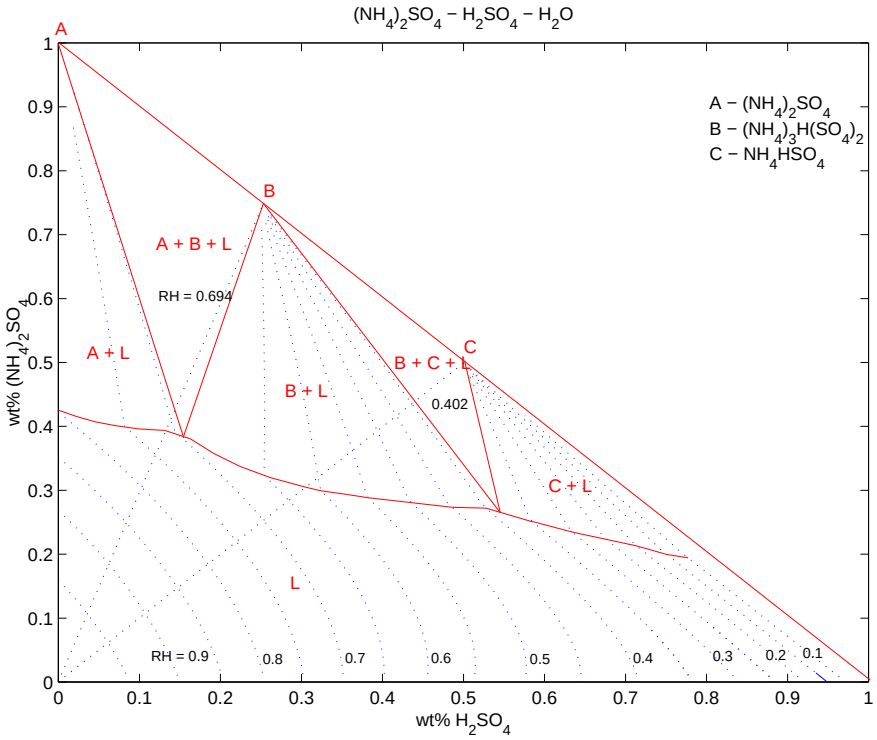
  $(NH_4)_2SO_4(s) \rightleftarrows 2NH_4^+(aq) + SO_4^{2-}(aq)$
  $(NH_4)_3H(SO_4)_2(s) \rightleftarrows 3NH_4^+(aq) + HSO_4^-(aq) + SO_4^{2-}(aq)$
  $NH_4HSO_4(s) \rightleftarrows NH_4^+(aq) + HSO_4^-(aq)$

5.2 Urban and Remote Continental Aerosols

The second example is two types of aerosols: urban and remote continental (Ref. 11), consisting of sulfate, nitrate and ammonium diluted in the air (with the specific ratio of H_2O-H_2SO_4-HNO_3-NH_3). Four solid phases (A, B, C and D) may possibly appear at equilibrium. They consist of the solids $(NH_4)_2SO_4$, $(NH_4)_3H(SO_4)_2$, NH_4HSO_4 and NH_4NO_3. Again, the chemical equilibrium reactions which are possible between the chemical components of the system are given in Table 3.

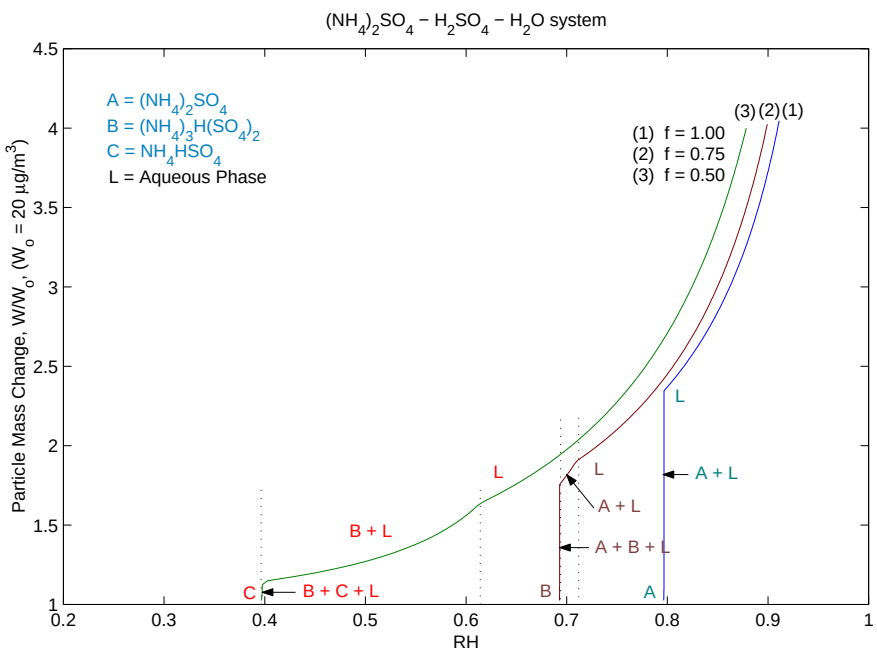
In Figures 4 and 5, the mass ratios of inorganic components and water in typical urban and remote continental aerosols are given as a function of the

Figure 1. Modeling of a sulfate aerosol. Reconstruction of the phase diagram at 25^oC with tracking of the presence of each solid phases. For each region of space the existing phases at equilibrium are represented.



relative humidity. Figures 4 and 5 illustrate clearly that the phase transitions are accurately tracked without any *a priori* knowledge of the existing phases. In Figures 6 and 7, the evolution of solid contents is investigated. For high relative humidity, no salts appear at the equilibrium. When the humidity decreases, the mass of salts increases until reaching a constant value for low relative humidity. The distribution of solid salts at low relative humidity is totally dependant on the inorganic feed composition.

Figure 2. Modeling of a sulfate aerosol. Evolution of the particle mass in function of the relative humidity RH. The creation/disappearance of a solid phase appears through a discontinuity in the derivatives of the trajectories. (f is the feed mole ratio: $\frac{n_{(NH_4)_2SO_4}}{n_{(NH_4)_2SO_4}+n_{H_2SO_4}}$ and W_0 is the amount of inorganic feed).



6 Conclusions

The modeling of atmospheric inorganic aerosols has been proposed in the framework of the canonical stoichiometry. The thermodynamic equilibrium corresponds to the minimum of the Gibbs free energy for a system involving a gas phase, an aqueous phase and solid salts. A numerical method for the solution of this optimization problem has been investigated. It is based on an active set/Newton method to take advantage of the constant chemical potentials for the solid phases. Numerical results have been presented to show the ability of our algorithm in the prediction of phase equilibria and its good numerical properties, especially in terms of convergence rate.

Figure 3. Modeling of a sulfate aerosol. Newton iteration at fixed RH = 0.85 in case of the inorganic feed B:$(NH_4)_3H(SO_4)_2$.

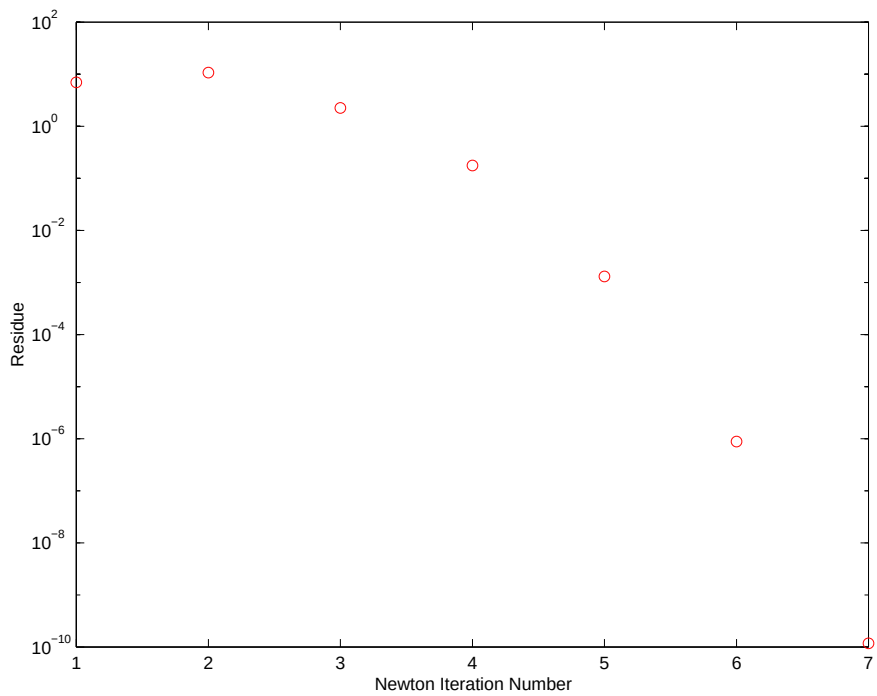


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Table 3. Chemical equilibrium reactions in sulfate/nitrate system.

- Vapor-Liquid Equilibrium:

$$H_2O(l) \rightleftarrows H_2O(g)$$
$$NH_3(l) \rightleftarrows NH_3(g)$$
$$H_2SO_4(l) \rightleftarrows H_2SO_4(g)$$
$$HNO_3(l) \rightleftarrows HNO_3(g)$$

- Speciation Equilibria:

$$HNO_3(l) \rightleftarrows H^+(aq) + NO_3^-(aq)$$
$$H_2SO_4(l) \rightleftarrows H^+(aq) + HSO_4^-(aq)$$
$$HSO_4^-(aq) \rightleftarrows H^+(aq) + SO_4^{2-}(aq)$$
$$NH_3(l) + H_2O(l) \rightleftarrows NH_4^+(aq) + OH^-(aq)$$
$$H_2O(l) \rightleftarrows H^+(aq) + OH^-(aq)$$

- Solid-Liquid Equilibria:

$$(NH_4)_2SO_4(s) \rightleftarrows 2NH_4^+(aq) + SO_4^{2-}(aq)$$
$$(NH_4)_3H(SO_4)_2(s) \rightleftarrows 3NH_4^+(aq) + HSO_4^-(aq) + SO_4^{2-}(aq)$$
$$NH_4HSO_4(s) \rightleftarrows NH_4^+(aq) + HSO_4^-(aq)$$
$$NH_4NO_3(s) \rightleftarrows NH_4^+(aq) + NO_3^-(aq)$$

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Figure 4. Deliquescence curve for sulfate/nitrate aerosol. Total $SO_4^{2-} = 9.143\mu g/m^3$, total $NO_3^- = 1.953\mu g/m^3$ and total $NH_4^+ = 3.400\mu g/m^3$.

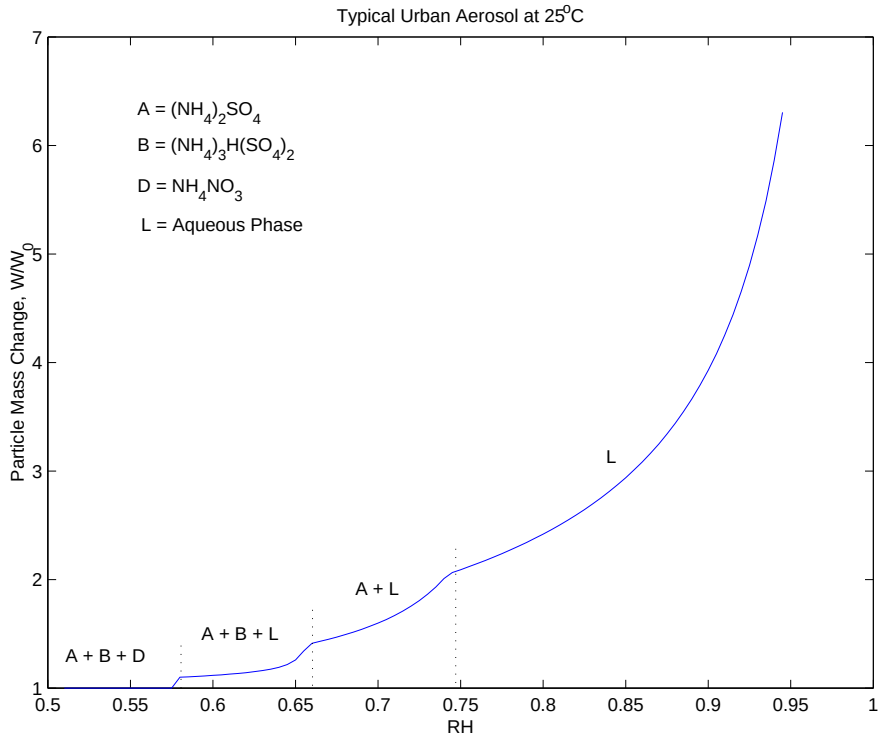

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Figure 5. Deliquescence curve for sulfate/nitrate aerosol. Total $SO_4^{2-} = 11.270\mu g/m^3$, total $NO_3^- = 0.145\mu g/m^3$ and total $NH_4^+ = 4.250\mu g/m^3$.

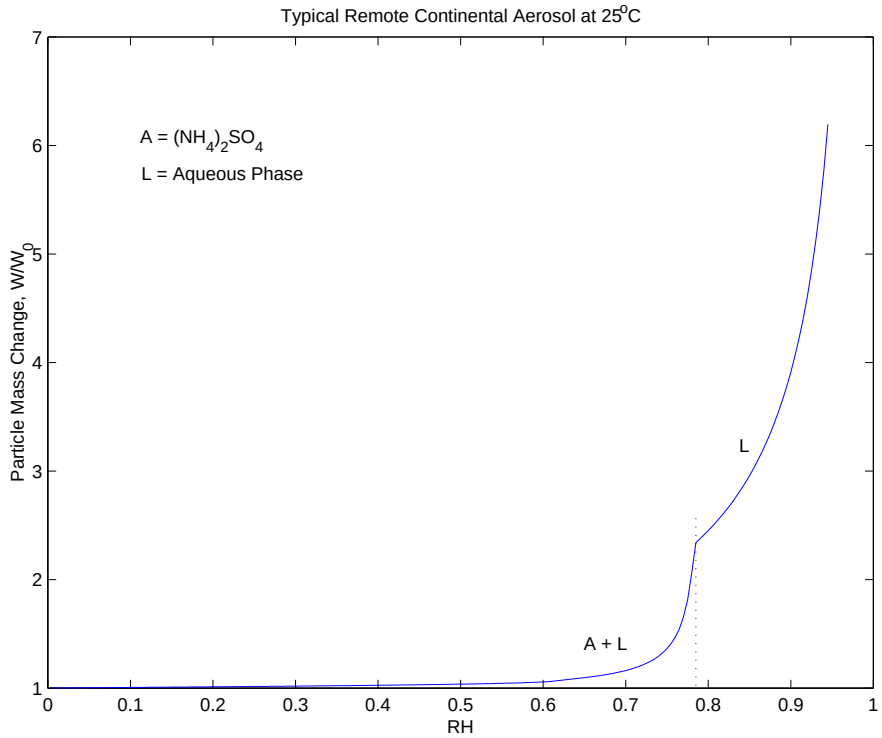

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Figure 6. Evolution of solid content of aerosol in Figure 4. $W_0 = 14.496 \mu g/m^3$.

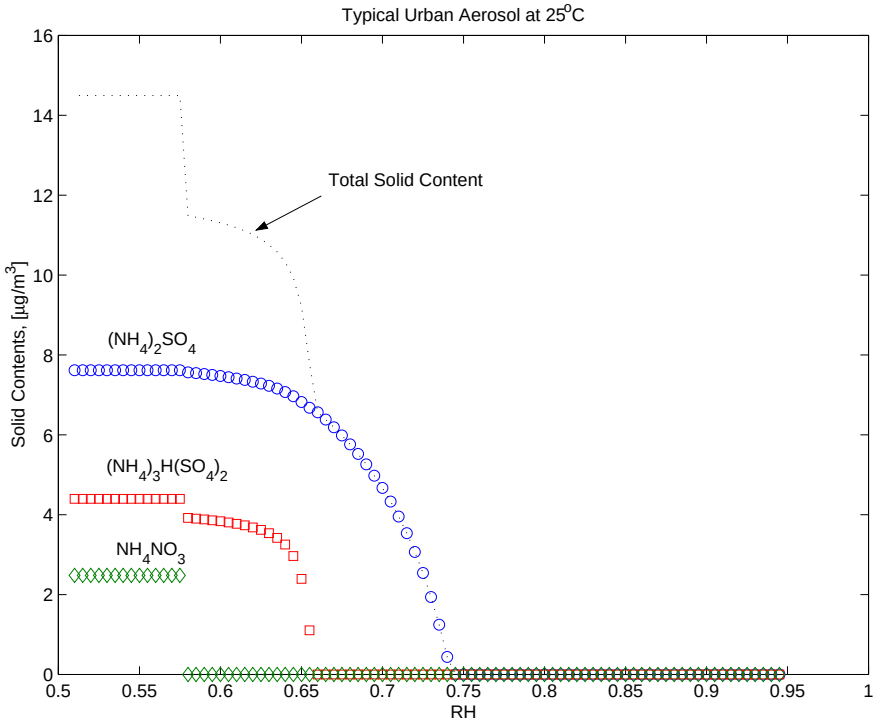

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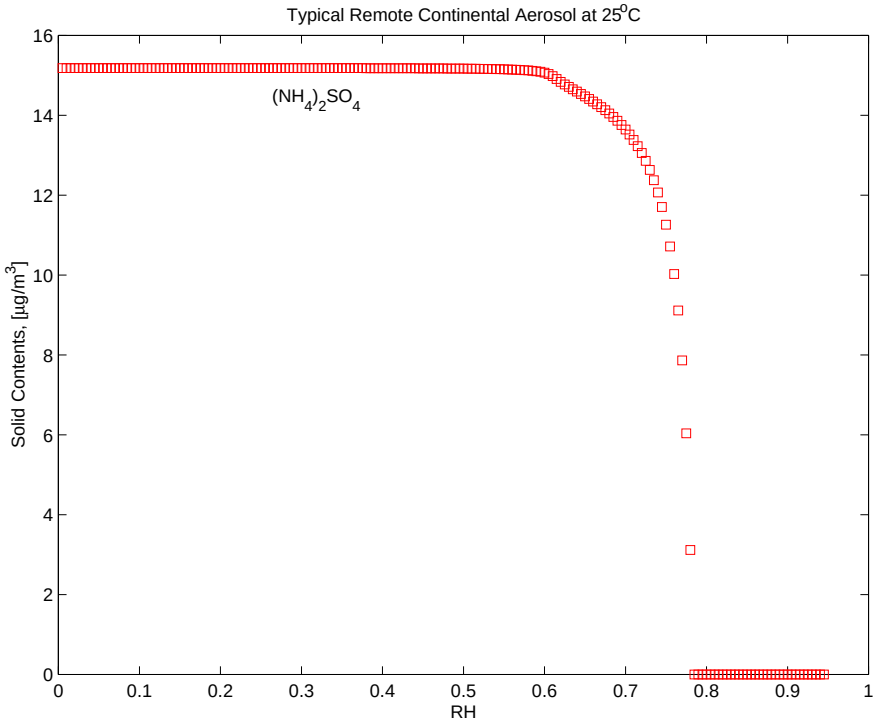
Figure 7. Evolution of solid content of aerosol in Figure 5. $W_0 = 15.665 \mu g/m^3$.



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