A PRIMAL-DUAL ACTIVE-SET METHOD AND ALGORITHM FOR CHEMICAL EQUILIBRIUM PROBLEM RELATED TO MODELING OF ATMOSPHERIC INORGANIC AEROSOLS

A Dissertation

Presented to

the Faculty of the Department of Department of Mathematics

University of Houston

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy

By

Trung Nguyen

December 2014

A PRIMAL-DUAL ACTIVE-SET METHOD AND ALGORITHM FOR CHEMICAL EQUILIBRIUM PROBLEM RELATED TO MODELING OF ATMOSPHERIC INORGANIC AEROSOLS

Trung Nguyen

APPROVED:

Dr. Jiwen He, Chairman
Department of Mathematics

Dr. Roland Glowinski
Department of Mathematics

Dr. Tsorng-Whay Pan
Department of Mathematics

Dr. William Fitzgibbon
Department of Technology

Dean, College of Natural Sciences and Mathematics

This dissertation is dedicated to my beloved wife, Hang Nguyen,

and my daughter, Minh-Trang Nguyen

Acknowledgements

I would like to thank my Ph.D. advisor, Dr. Jiwen He, for his encouragement and guidance throughout this work. His enormous experience in mathematics and innovative ideas was crucial to the success of the projects we worked on. I appreciate his efforts and positive outlook which kept me motivated throughout this journey. He gave me the freedom to learn and work independently and, at the same time, kept me focused and stay on track. He was very supportive and provided valuable advice throughout my research. I would not have succeeded in this endeavor without his tireless patience, encouragement, and trust.

I would also like to thank my committee members, Dr. Roland Glowinski, Dr. William Fitzgibbon, and Dr. Tsorng-Whay Pan for being part of my dissertation committee and providing valuable suggestions.

I greatly acknowledge the financial, academic, and technical support from the Department of Mathematics at the University of Houston. I would like to extend sincere thanks to Dr. Jeffrey Morgan for his support and inspiration. I would also like to thank all of the faculty and staff of the department.

A PRIMAL-DUAL ACTIVE-SET METHOD AND ALGORITHM FOR CHEMICAL EQUILIBRIUM PROBLEM RELATED TO MODELING OF ATMOSPHERIC INORGANIC AEROSOLS

An Abstract of a Dissertation

Presented to

the Faculty of the Department of Department of Mathematics

University of Houston

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy

By

Trung Nguyen

December 2014

Abstract

In this dissertation, we studied a general equilibrium model for multiphase multicomponent inorganic atmospheric aerosols. We developed the thermodynamic model to predict the phase transition and multistage growth phenomena of inorganic aerosols. 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 for solving the *Karush-Kuhn-Tucker* conditions is one of the main focus of the model. We applied an active set and the Newton method to compute the minimum of energy and determined if solid salts exist or not at the equilibrium.

We presented that the model were set up based on the mass balance equations and the minimization of the Gibbs Free Energy. We developed a mathematical framework for modeling solid-liquid equilibrium reactions that was based on the canonical stoichiometry of the inorganic aerosols. We showed detailed work on how to model a typical system of inorganic aerosols at equilibrium. We demonstrated how the active set method was applied in two modeling problems. One was for general chemical equilibrium problem. Another one was to extend the current modeling problem to investigate the system at fixed relative humidity.

Numerical results of the model are included to show the efficiency of the algorithm for the prediction of multiphase multireaction chemical equilibria. We used typical inorganic aerosol systems for this purpose. One system was the sulfate aerosols which included ammonium sulfate $(NH_4)_2SO_4$, sulfuric acid H_2SO_4 and water H_2O. Another system had two type of aerosols: urban and remote continental. This system consisted of water H_2O, sulfuric acid H_2SO_4, nitric acid HNO_3, and ammonia NH_3. From the results, we demonstrated that the model was capable of computing

phase behavior of inorganic aerosols efficiently and rigorously. It also computed the deliquescent behavior of the system.

Contents

1 Introduction **1**

2 Background **5**

2.1 Chemical Engineering Concept 5

2.1.1 Basic Stoichiometric Concepts 5

2.1.2 Chemical Potential And Standard States 12

2.1.3 The Equilibrium Constant and Its Relation to Gibbs Free Energy 13

2.2 Numerical Optimization concept 15

2.2.1 Karush-Kuhn-Tucker Condition 15

2.2.2 Active Set Method 18

2.2.3 Newton Method 27

3 Modeling Problems **31**

3.1 Modeling of Inorganic Aerosols 31

3.1.1 Chemical Equilibrium Formulation of the Problem 31

3.2 Description of the Problem and Optimality Conditions 35

3.2.1 Optimality Conditions and the Karush-Kuhn-Tucker System . 35

3.2.2 Chemical Equilibrium Problem at Fixed Relative Humidity . . 40

4 Methods and Algorithm **45**

4.1 Phase Stability Criterion and Active Set 45

4.2 Inertia Theory 47
4.3 Primal-Dual Active Set Method 51
4.4 Active Set Method algorithms 57
4.5 Computation of Newton Direction 61

5 Results **71**
5.1 Sulfate Aerosols 72
5.2 Urban and Remote Continental Aerosols 73

6 Conclusions **82**

List of Figures

5.1 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. . . 74

5.2 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). 75

5.3 Modeling of a sulfate aerosol. Newton iteration at fixed RH = 0.85 in case of the inorganic feed B:$(NH_4)_3H(SO_4)_2$. 76

5.4 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 $NH_4^+ = 3.400\mu g/m^3$. 78

5.5 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 $NH_4^+ = 4.250\mu g/m^3$. 79

5.6 Evolution of solid content of aerosol in Figure 5.4. $W_0 = 14.496\mu g/m^3$. 80

5.7 Evolution of solid content of aerosol in Figure 5.5. $W_0 = 15.665\mu g/m^3$. 81

List of Tables

2.1 Chemical equilibrium reactions in the sulfate aerosols are summarized below. The first class denotes the decomposition reactions and possible ionic reactions; the second class describes the reactions with phase changes which may lead to the solid formation. 9

4.1 Active set/Newton method: summary of the algorithm. 60

5.1 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 describes the reactions with phase changes which may lead to the formation of a solid. 72

5.2 Chemical equilibrium reactions in sulfate/nitrate system. 77

Chapter 1

Introduction

The ability to predict the phase transition in multireaction chemical equilibrium is desirable in chemical engineering and atmospheric science. For the last three decades, a series of thermodynamic modules, such as such as EQUIL [7], MARS [33], SEQUILIB [32], SCAPE [22, 23], SCAPE2 [21, 27], EQUISOLV II [18, 19, 20], and ISORROPIA [28, 29], 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, these modules may fail to accurately predict the phase state, composition, and the multistage growth phenomena of inorganic aerosols [5, 6].

Other thermodynamic models that are based on the *minimization of the Gibbs Free Energy*, such as GFEMN [6] and AIM [8, 10, 11, 25, 36], which implicitly predict phase transition and multistage aerosol growth without any *a priori* knowledge of the behavior of inorganic aerosols. Such direct minimization of the Gibbs Free Energy is computationally intensive and could result in making air quality models unfeasible [5, 38].

This dissertation describes a *primal-dual active set* algorithm for the efficient and accurate prediction of the phase transition and multistage growth phenomena of inorganic aerosols. The mathematical framework for modeling solid-liquid equilibrium reactions is based on the *canonical stoichiometry* of inorganic aerosols. The canonical form is applied to the model 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.

The principal features of the algorithm can be summarized as following:

- The algorithm applies Newton 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* is used 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 so 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-negative characteristic 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).

- To avoid the negative values and inaccurate 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 dissertation is the following: Chapter 2 introduces background knowledge in chemical engineering and mathematics. For the chemical engineering background, this chapter covers stoichiometric coefficients and equations, chemical potential, and Gibbs Free Energy. For the mathematics background, it discusses the Karush-Kuhn-Tucker condition, active set method, and Newton method. These

concepts are a foundation for the modeling of inorganic aerosol problems. In Chapter 3, the steps of the mathematical modeling of inorganic aerosols are presented. In Chapter 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 presented for solving this minimization problem. Numerical results are presented in Chapter 5 to illustrate the efficiency of the model. Finally, Chapter 6 consists in the conclusions.

Chapter 2

Background

2.1 Chemical Engineering Concept

2.1.1 Basic Stoichiometric Concepts

Consider the following general reaction

$$bB + cC + \ldots \rightleftharpoons sS + tT + \ldots, \tag{2.1}$$

where $b, c, s,$ and t are the stoichiometric coefficients of the species $B, C, S,$ and T respectively. We define generalized stoichiometric coefficients υ_i for the above reaction by rewriting it in the following manner:

$$0 = \upsilon_B B + \upsilon_C C + \ldots + \upsilon_S S + \upsilon_T T + \ldots , \tag{2.2}$$

where

$$\begin{aligned} \upsilon_B &= -b, \qquad \upsilon_S = s, \\ \upsilon_C &= -c, \qquad \upsilon_T = t. \end{aligned} \tag{2.3}$$

In chemical reaction, the generalized stoichiometric coefficients are defined as positive quantities for the products and as negative quantities for the reactants. The coefficients of species that are neither produced nor consumed by the indicated reaction are taken to be zero. The equation (2.2) can be further generalized as follows:

$$\sum_i \upsilon_i A_i = 0, \tag{2.4}$$

where the sum is taken over all components A_i present in the system.

Example 1 ***(Single stoichiometric equation)***

Let us look at the ionic decomposition of a weak carbonic acid in an aqueous solution:

$$H_2CO_3 = 2H^+ + CO_3^{2-}$$

.

Alternately, this equation can be written in stoichiometric form as follow

$$-H_2CO_3 + 2H^+ + CO_3^{2-} = 0, \tag{2.5}$$

where the stoichiometric coefficients are

$$\upsilon_{CO_3^{2-}} = 1; \quad \upsilon_{H^+} = 2; \quad \upsilon_{H_2CO_3} = -1.$$

If we denote:

$$A_1 = H_2CO_3, \qquad A_2 = H^+, \qquad A_3 = CO_3^{2-},$$

then the stoichiometric equation for (2.5) is written in term of a generalized equation (2.4) as follows:

$$-A_1 + 2A_2 + A_3 = 0. \tag{2.6}$$

For the case of multiple simultaneous reactions, equation (2.4) is extended to

$$\sum_{1}^{S} \upsilon_{ki} A_i = 0, \qquad k = 1, 2, \ldots, R \tag{2.7}$$

where R is the numbers of reactions. The sum is taken over the total of S component species A_i present in the system.

Let us look at an example of sulfate aerosols in the atmosphere where chemical reactions can take place. We studied how the stoichiometric equations were written for the system.

Example 2 ***(simultaneous reactions and stoichiometric coefficient matrix)*** *Consider an aerosol system of sulfate particles which include three species: ammonium sulfate* $(\mathrm{NH_4})_2\mathrm{SO_4}$*, sulfuric acid* $\mathrm{H_2SO_4}$ *and water* $\mathrm{H_2O}$*. At equilibrium, the system can possibly form three solids:*

$$
\begin{array}{ll}
A : (NH_4)_2SO_4 & \textit{Ammonium sulfate,} \\
B : (NH_4)_3H(SO_4)_2 & \textit{Triammonium hydrogen disulphate,} \\
C : (NH_4)HSO_4 & \textit{Ammonium hydrogen sulfate.}
\end{array}
$$

The chemical reactions which may take place in the system are expressed in term of the chemical components in Table 2.1.

Table 2.1: Chemical equilibrium reactions in the sulfate aerosols are summarized below. The first class denotes the decomposition reactions and possible ionic reactions; the second class describes the reactions with phase changes which may lead to the solid formation.

- ***Part I**: Decomposition Reactions and other Ionic Reactions in aqueous phase:*

$H_2SO_4(l)$	$\rightleftarrows$	$H^+(aq) + HSO_4^-(aq)$
$HSO_4^-(aq)$	$\rightleftarrows$	$H^+(aq) + SO_4^{2-}(aq)$
$(NH_4)_2SO_4(s)$	$\rightleftarrows$	$2NH_4^+(aq) + SO_4^{2-}(aq)$
$H_2O(l)$	$\rightleftarrows$	$H^+(aq) + OH^-(aq)$
$NH_4^+(aq) + OH^-(aq)$	$\rightleftarrows$	$NH_3(g) + H_2O(l)$

- ***Part II**: Composition reactions (solid formation):*

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

For simplification, we will form the stoichiometric coefficient matrix for ***Part I*** *of Table 2.1 first and the whole system at the end of the example.*

If we define the chemical components A_i as follows,

$$
\begin{array}{lll}
A_1 = \mathrm{H_2SO_4}, & A_2 = \mathrm{H^+}, & A_3 = \mathrm{HSO_4^-}, \\
A_4 = \mathrm{SO_4^{2-}}, & A_5 = \mathrm{(NH_4)_2SO_4}, & A_6 = \mathrm{NH_4^+}, \\
A_7 = \mathrm{H_2O}, & A_8 = \mathrm{OH^-}, & A_9 = \mathrm{NH_3}, \\
A_{10} = \mathrm{(NH_4)_3H(SO_4)_2}, & A_{11} = \mathrm{NH_4HSO_4}, &
\end{array}
$$

then the equations for the "Ionic Decomposition Reactions and Ionic Reactions" portion of table (2.1) can expanded from equation (2.7) to the following:

$$
\begin{bmatrix}
-A_1 + A_2 + A_3 & & & & & = 0 \\
& A_2 - A_3 + A_4 & & & & = 0 \\
& & A_4 - A_5 + 2A_6 & & & = 0 \\
& A_2 & & - A_7 + A_8 & & = 0 \\
& & & & - \ A_6 + A_7 - A_8 + A_9 & = 0
\end{bmatrix}
\tag{2.8}
$$

System of equations (2.8) is referred as stoichiometric equations where chemical reactions are formulated in their component forms instead of as species.

The stoichiometric coefficient matrix of the equation system (2.8) will be:

$$\begin{bmatrix} -1 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & -1 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & -1 & 2 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & -1 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 & 1 & -1 & 1 \end{bmatrix} \tag{2.9}$$

Similarly, by adding ***Part II*** *of the Table 2.1, the stoichiometric coefficient matrix of the whole system is:*

$$\begin{bmatrix} -1 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & -1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & -1 & 2 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & -1 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 & 1 & -1 & 1 & 0 & 0 \\ 0 & 0 & 0 & -1 & 1 & -2 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & -1 & 0 & -3 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & -1 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \tag{2.10}$$

2.1.2 Chemical Potential And Standard States

The basic criterion for the establishment of chemical reaction equilibrium is that

$$\sum_i \upsilon_i \mu_i = 0, \tag{2.11}$$

where the μ_i are the chemical potentials of the various species in the reaction mixture. If r numbers of reactions occur in the system and equilibrium is established with respect to each of these reactions, it is required that

$$\sum_i \upsilon_{ik} \mu_i = 0 \quad \text{where } k = 1, 2, \ldots, r. \tag{2.12}$$

The chemical potential μ_i of species i is related to its activity a_i by

$$\mu_i = \mu_i^0 + RT \; ln \, a_i, \tag{2.13}$$

where R is the gas constant,

T is the absolute temperature,

μ_i^0 is the standard chemical potential of species i in a reference state where its activity is taken as unity.

The choice of the standard state is based primarily on experimental data and reproducibility. The temperature of the standard state is the same as that of the system under investigation.

2.1.3 The Equilibrium Constant and Its Relation to Gibbs Free Energy

The equilibrium criteria for given chemical reaction is that the Gibbs Free Energy $\triangle G$ change associated with the progress of the reaction be zero.

$$\triangle G = \sum_i \upsilon_i \mu_i = 0. \tag{2.14}$$

Furthermore, the standard Gibbs Free Energy $\triangle G^0$ change for a reaction refers to the process wherein the reaction proceeds isothermally, starting with stoichiometric quantities of reactants each in its standard state of unit activity and ending with products each at unit activity. In general, it is nonzero and given by

$$\triangle G^0 = \sum_i \upsilon_i \mu_i^0. \tag{2.15}$$

Subtracting the equation (2.15) from the equation (2.14) gives

$$\triangle G - \triangle G^0 = \sum_i \upsilon_i \left(\mu_i - \mu_i^0\right). \tag{2.16}$$

Equation (2.16) can be rewritten in term of the activities in equation (2.13) as follows:

$$\triangle G - \triangle G^0 = RT \sum_i \nu_i \, ln \, a_i = RT \, ln \left(\prod_i a_i^{\upsilon_i} \right). \tag{2.17}$$

When the system reaches equilibrium stage, we have $\triangle G = 0$. Equation (2.17) becomes:

$$\triangle G^0 = -RT\, ln \left(\prod_i a_i^{v_i} \right). \tag{2.18}$$

We defined the equilibrium constant K_a at temperature T as follows:

$$K_a = \prod_i a_i^{v_i}, \tag{2.19}$$

where the subscript "a" is used to emphasize that the equilibrium constant is written in relation with the activities.

Thus, from equation (2.18), and equation (2.19), the relation of Gibbs Free Energy and the equilibrium constant is given by:

$$K_a = e^{-\triangle G^0/RT}. \tag{2.20}$$

Example 3 ***(Equilibrium Constant)***

Let us consider a general chemical reaction of the form:

$$bB + cC + \ldots \rightleftharpoons sS + tT + \ldots ,$$

From equation(2.17), we have:

$$\triangle G - \triangle G^0 = RT\, ln \left(\prod_i a_i^{v_i} \right) = RT\, ln \left[\frac{a_S^s a_T^t \ldots}{a_B^b a_C^c \ldots} \right]. \tag{2.21}$$

At equilibrium, we have $\triangle G = 0$. Equation (2.21) becomes:

$$\triangle G^0 = -RT\, lnK_a, \tag{2.22}$$

where $K_a = \dfrac{a_S^s a_T^t \cdots}{a_B^b a_C^c \cdots}$ *is the equilibrium constant.*

2.2 Numerical Optimization concept

2.2.1 Karush-Kuhn-Tucker Condition

Consider a nonlinear optimization problems (NLP) of the form

$$\underset{x \in \mathbb{R}^n}{minimize} \qquad f(x), \tag{2.23a}$$

$$subject\, to \quad h(x) = 0, \tag{2.23b}$$

$$g(x) \leq 0, \tag{2.23c}$$

where the function $f:\ \mathbb{R}^n \to \mathbb{R}$ is the objective functional, the functions $h:\ \mathbb{R}^n \to \mathbb{R}^m$ and $g:\ \mathbb{R}^n \to \mathbb{R}^p$ describe the equality and inequality constraints respectively.

Definition 2.2.1 **(Feasible Set)**

The feasible set is the set of points that satisfy the equality and inequality constraints of the NLP.

$$\mathcal{F} \quad := \{\ x \in \mathbb{R}^n |\ h(x) = 0,\ g(x) \leq 0\ \}\,. \tag{2.24}$$

The elements of the feasible set f are referred to as feasible points. In terms of the feasible set, the NLP (2.23) can be written in the more compact form

$$\underset{\mathcal{F}}{minimize} \quad f(x).$$

The Lagrangian functional $\mathcal{L} := \mathbb{R}^n \times \mathbb{R}^m \times \mathbb{R}^p \to \mathbb{R}$ associated with the NLP (2.23) is defined

$$\mathcal{L}(x, \lambda, \mu) \ := f(x) + \lambda^T h(x) + \mu^T g(x). \tag{2.25}$$

Definition 2.2.2 **(Active Set and Working Set)**

Let $x \in \mathcal{F}$, the active set $\mathcal{I}_{ac}(x)$ at x is the set of active inequality constraints at x

$$\mathcal{I}_{ac}(x) := \{1 \leq i \leq p \mid g_i(x) = 0\}. \tag{2.26}$$

Its complement $\mathcal{I}_{ia}(x) := \{i, \ldots, p\} \setminus \mathcal{I}_{ac}(x)$ is referred to as the set of inactive inequality constraints.

Let $\mathcal{E}(x)$ be the equality constraint set.

$$\mathcal{E}(x) := \{1 \leq i \leq m \mid h_i(x) = 0\}. \tag{2.27}$$

The working set is defined as the union of equality constraint set and active set.

$$\mathcal{W}(x) := \mathcal{E}(x) \cup \mathcal{I}_{ac}(x). \tag{2.28}$$

Definition 2.2.3 **(Linear Independence Constraint Qualification)**

Let $\mathcal{I}_{ac}(x^*)$ be the set of active inequality constraints at x^* and $x^* \in \mathcal{F}$. Then, the Linear Independence Constraint Qualification (LICQ) is satisfied at x^* if the set of active constraint gradients,

$$\{\nabla h_1(x^*), \ldots, \nabla h_m(x^*), \nabla g_i(x^*), i \in \mathcal{I}_{ac}(x^*)\}, \tag{2.29}$$

is linearly independent.

Theorem 2.2.4 (Karush-Kuhn-Tucker conditions)

Assume that $x^* \in \mathcal{F}$ is the local solution of the NLP (2.23) and that the LICQ is satisfied at x^*. Then, there exist Lagrange multipliers $\lambda^* \in \mathbb{R}^m$ and $\mu^* \in \mathbb{R}^p$ such that the following conditions hold true at (x^*, λ^*, μ^*)

$$\begin{aligned}
\nabla_x \mathcal{L}(x^*, \lambda^*, \mu^*) &= 0, && \text{(2.30a)}\\
h_i(x^*) &= 0, \quad 1 \le i \le m, && \text{(2.30b)}\\
g_i(x^*) &\le 0, \quad 1 \le i \le p, && \text{(2.30c)}\\
\mu_i^* &\ge 0, \quad 1 \le i \le p, && \text{(2.30d)}\\
\mu_i^* g_i(x^*) &= 0, \quad 1 \le i \le p. && \text{(2.30e)}
\end{aligned}$$

The Karush-Kuhn-Tucker (KKT) conditions are also referred to as the first order optimality conditions. The proof of the KKT theorem (2.30) can be found in many standard textbook. The condition $\mu_i^* g_i(x^*) = 0$, is called the complementary condition since it essentially says that at least one of the μ^* or $g_i(x^*)$ must be zero for

each $i = 1, 2, \ldots, p$. The complementary condition is sometime written in the form $\mu^T g(x) = 0$

Definition 2.2.5 **(Strick Complementary Condition)**

Let $x^* \in \mathcal{F}$ be a local solution of the NLP (2.23) and λ^*, μ^* be the Lagrange multipliers satisfying the KKT conditions (2.30). Then, the strict complementarity holds true if

$$\mu_i^* > 0 \quad , \quad i \in I_{ac}(x^*).$$

2.2.2 Active Set Method

Consider solving the NLP:

$$\underset{x \in \mathbb{R}^n}{minimize} \qquad f(x), \tag{2.31a}$$

$$subject\,to \quad h(x) = 0, \tag{2.31b}$$

$$g(x) \leq 0. \tag{2.31c}$$

The idea of the active set method is trying to solve the above NLP by only considering the equality constraints. First, the inequality constraints are partitioned into two group: an equality constraint group and an inequality constraint group. The inequality constraints will not be involved during the main calculation and are simply ignored.

The necessary conditions (KKT conditions) for the NLP problem are:

$$
\begin{aligned}
\nabla_x \mathcal{L}\left(x^*, \lambda^*, \mu^*\right) &= \nabla f(x) + \lambda^T \nabla h(x) + \mu^T \nabla g(x) = 0, && (2.32a)\\
h_i(x^*) &= 0, \quad 1 \leq i \leq m, && (2.32b)\\
g_i(x^*) &\leq 0, \quad 1 \leq i \leq p, && (2.32c)\\
\mu_i^* &\geq 0, \quad 1 \leq i \leq p, && (2.32d)\\
\mu_i^* g_i(x^*) &= 0, \quad 1 \leq i \leq p. && (2.32e)
\end{aligned}
$$

Let $\mathcal{I}_{ac}(x)$ and $\mathcal{I}_{ia}(x)$ denote the active and inactive set of $f(x)$ as in definition(2.26). The KKT conditions (2.32) can be written in term of the active set:

$$
\begin{aligned}
\nabla_x \mathcal{L}\left(x^*, \lambda^*, \mu^*\right) &= \nabla f(x^*) + \lambda^T \nabla h(x^*) + \mu^T \nabla g(x^*) = 0, && (2.33a)\\
h_i(x^*) &= 0, \quad 1 \leq i \leq m && (2.33b)\\
g_i(x^*) &= 0, \quad i \in \mathcal{I}_{ac}(x), && (2.33c)\\
\mu_i^* &\geq 0, \quad i \in \mathcal{I}_{ac}(x), && (2.33d)\\
g_i(x^*) &< 0, \quad i \in \mathcal{I}_{ia}(x), && (2.33e)\\
\mu_i^* &= 0, \quad i \in \mathcal{I}_{ia}(x). && (2.33f)
\end{aligned}
$$

Let us look at the following active set optimization problem where we only take the equality constraints of the NLP into account and ignore the inequality constraints:

$$\underset{x\in\mathbb{R}^n}{minimize} \qquad f(x), \tag{2.34a}$$

$$subject\,to \quad h_i(x) = 0, \quad 1 \leq i \leq m, \tag{2.34b}$$

$$g_i(x) = 0, \quad i \in \mathcal{I}_{ac}(x). \tag{2.34c}$$

Next, we take the KKT conditions of (2.34) and compare them to the conditions of the NLP:

$$\nabla_x \mathcal{L}\left(x^*, \lambda_1^*, \lambda_2^*\right) = \nabla f(x^*) + \lambda^T \nabla h(x^*) + \mu^T \nabla g(x^*) = 0, \tag{2.35a}$$

$$h_i(x^*) = 0, \quad 1 \leq i \leq m, \tag{2.35b}$$

$$g_i(x^*) = 0, \quad i \in \mathcal{I}_{ac}(x). \tag{2.35c}$$

We observe that the the first three KKT condition of the NLP (2.33) and the active set optimization problem (2.35) are the same. The remaining condition guarantee that the inactive constraints are satisfied, the Lagrange multipliers are positive and the complementary condition is preserved. Therefore, the solutions of the active set optimization problem are also the solution of the one of the NLP provided that the last tree KKT condition of the NLP problem are satisfied. This observation is essentially the main idea of the active set method.

In other words, the active set method approach is to replace the original problem by the corresponding problem that only has the equality constraints, the active set problem. Alternatively, suppose an active set was obtained and the corresponding

equality constrained problem solved. If the other constraints were satisfied and the Lagrange multipliers turned out to be non-negative, then solution would be correct.

The algorithm of the active set methods is to define at each step, or at each phase, a set of constraints, known as the working set, that is to be treated as the active set. The working set is chosen to be a subset of the constraints that are actually active at the current point, and hence the current point is feasible for the working set. The algorithm then proceeds to move on the surface defined by the working set of constraints to an improved point. At this new point the working set may be changed.

Overall, then, an active set method consists of the following components:

1. Determination of a current working set that is a subset of the current active constraints, and
2. determine the movement on the surface defined by the working set to an improved point.

There are several methods for determining the movement on the surface defined by the working set. This surface is sometime called the working surface. The direction of movement is generally determined by first-order or second-order approximations of the functions at the current point in a manner similar to that for unconstrained problems. The asymptotic convergence properties of active set methods depend entirely on the procedure for moving on the working surface. Since near the solution, the working set is generally equal to the correct active set, and the process simply moves successively on the surface determined by those constraints.

The active set strategy has the following guidelines: The overall scheme is to develop a systematic method for dropping and adding constraints from the working set.

- One starts with a given working set and initial guess
- Then one begins minimizing over the corresponding working surface. If new constraint boundaries are encountered, they may be added to the working set, but no constraints are dropped from the working set at this stage. Finally, a point is obtained that minimizes f with respect to the current working set of constraints. The corresponding Lagrange multipliers are determined. And if they are all non-negative, the solution is optimal. Otherwise, one or more constraints with negative Lagrange multipliers are dropped from the working set.
- The procedure is re-initiated with this new working set, and the objective function f will strictly decrease on the next step.

Example 4 ***(Active Set strategies for convex Quadratic Programming problem)***

Let us consider an example of how the primal active set method is applied to the constrained Quadratic Programming (QP) problem:

$$\underset{x\in\mathbb{R}^n}{minimize} \quad f(x) := \frac{1}{2}x^T Bx - x^T b, \tag{2.36a}$$

$$subject\,to \qquad Cx = c, \tag{2.36b}$$

$$Ax \leq d, \tag{2.36c}$$

where $f \in \mathbb{R}^n$ *,* $B \in \mathbb{R}^{n\times n}$ *is symmetric positive definite,* $C \in \mathbb{R}^{m\times n}$*,* $A \in \mathbb{R}^{p\times n}$ *and* $b \in \mathbb{R}^n$*,* $c \in \mathbb{R}^m$*, and* $d \in \mathbb{R}^p$*. The inequality constraints* $Ax \leq d$ *can be written as follows*

$$a_i^T x \leq d_i \qquad , \qquad 1 \leq i \leq m. \tag{2.37}$$

The idea of active set methods is to apply iterative procedure. For a given iterate $x^{(\nu)}$*,* $\nu \geq 0$ *in feasible set* $\mathcal{F}$*, we determine the active set*

$$\mathcal{I}_{ac}\left(x^{(\nu)}\right) = \{1 \ldots p\},$$

and only consider the corresponding constraints as equality constraints, whereas the remaining inequality constraints are disregarded.

$$\underset{x\in\mathbb{R}^n}{minimize} \qquad f(x) := \frac{1}{2}x^T Bx - x^T b, \tag{2.38a}$$

$$subject\,to \qquad Cx = c, \tag{2.38b}$$

$$a_i^T x = d_i, \quad i \in \mathcal{I}_{ac}\left(x^{(\nu)}\right). \tag{2.38c}$$

The working set is defined

$$\mathcal{W} = \mathcal{I}_{ac}\left(x^{(\nu)}\right) \cup \mathcal{E}\left(x^{(\nu)}\right), \tag{2.39}$$

where $\mathcal{E}\left(x^{(\nu)}\right) = \{1 \ldots m\}$*.*

If we denote

$$p = x^{(\nu)} - x, \qquad b^{(\nu)} = Bx^{(\nu)} - b,$$

the function $f(x)$ in equation (2.38) becomes:

$$f(x) = f\left(x^{(\nu)} - p\right) = \frac{1}{2}p^T Bp - \left(b^{(\nu)}\right)^T p + g, \tag{2.40}$$

where $g := \frac{1}{2}\left(x^{(\nu)}\right)^T Bx^{(\nu)} - p^T x^{(\nu)}$ is a constant term. Since we can drop g from the objective without changing the solution of the problem, we can write the QP subproblem to be solved at the $(\nu+1)$ iteration step as follows:

$$\underset{x\in\mathbb{R}^n}{minimize} \quad f(p) := \frac{1}{2}p^T Bp - \left(b^{(\nu)}\right)^T p, \tag{2.41a}$$

$$subject\,to \qquad Cp = 0, \tag{2.41b}$$

$$a_i^T p = 0, \quad i \in \mathcal{I}_{ac}\left(x^{(\nu)}\right). \tag{2.41c}$$

If we denote the solution of (2.41) to be $p^{(\nu)}$ then new iterate $x^{(\nu+1)}$ is obtained as follows

$$x^{(\nu+1)} = x^{(\nu)} - \alpha_\nu p^{(\nu)} \quad , \quad \alpha_\nu \in [0,1], \tag{2.42}$$

where α_ν is chosen such that $x^{(\nu+1)}$ stay feasible. In particular, let us compute the value of α_ν. For $i \in \mathcal{I}_{ac}\left(x^{(\nu)}\right)$, we have from (2.42) that

$$a_i^T x^{(\nu+1)} = a_i^T x^{(\nu)} - \alpha_\nu a_i^T p^{(\nu)} = a_i^T x^{(\nu)} \leq d_i. \tag{2.43}$$

Thus the constraints are satisfied regardless the value of α_ν. Therefore, we only compute the value of α_ν for $i \notin \mathcal{I}_{ac}\left(x^{(\nu)}\right)$.

If $a_i^T p^{(\nu+1)} \geq 0$ for $i \notin \mathcal{I}_{ac}\left(x^{(\nu)}\right)$, it follows that

$$a_i^T x^{(\nu+1)} = a_i^T x^{(\nu)} - \alpha_\nu a_i^T p^{(\nu)} \leq a_i^T x^{(\nu)} \leq d_i. \tag{2.44}$$

Also, if $a_i^T p^{(\nu+1)} < 0$ for $i \notin \mathcal{I}_{ac}\left(x^{(\nu)}\right)$, it have

$$a_i^T x^{(\nu+1)} = a_i^T x^{(\nu)} - \alpha_\nu a_i^T p^{(\nu)} \leq d_i, \tag{2.45}$$

which requires that

$$\alpha_\nu \leq \frac{a_i^T x^{(\nu)} - d_i}{a_i^T p^{(\nu)}}. \tag{2.46}$$

Consequently, in order to guarantee feasibility, we need to choose α_ν such that

$$\alpha_\nu := min\left(1, \min_{a_i^T p^{(\nu)} < 0,\, i \notin \mathcal{I}_{ac}\left(x^{(\nu)}\right)} \frac{a_i^T x^{(\nu)} - d_i}{a_i^T p^{(\nu)}}\right). \tag{2.47}$$

We call the constraints i for which the minimum in (2.47) is achieved the blocking constraints $\mathcal{I}_{bl}$.

$$\mathcal{I}_{bl}\left(p^{(\nu)}\right) := \left\{ i \notin \mathcal{I}_{ac}\left(x^{(\nu)}\right) \mid a_i^T p^{(\nu)} < 0, \min_{i \notin \mathcal{I}_{ac}\left(x^{(\nu)}\right)} \frac{a_i^T x^{(\nu)} - d_i}{a_i^T p^{(\nu)}} \right\}. \tag{2.48}$$

Note that for $i \in \mathcal{I}_{bl}\left(p^{(\nu)}\right)$, we have

$$a_i^T x^{(\nu+1)} = a_i^T x^{(\nu)} - \alpha_\nu a_i^T p^{(\nu)} = d_i. \tag{2.49}$$

If $\alpha_k < 1$, the step along p_k was blocked by some constraints that are not in $\mathcal{I}_{ac}\left(x^{(\nu)}\right)$ a new active set $\mathcal{I}_{ac}\left(x^{(\nu+1)}\right)$ is constructed by adding the most restrictive blocking constraints to $\mathcal{I}_{ac}\left(x^{(\nu)}\right)$. The working constraints $\mathcal{W}$ is updated accordingly.

We can obtain further information with respect to a proper specification of the set of active constraints by systematically checking the KKT conditions:

Assume that $p(\nu) = 0$ is the solution of the QP sub-problem (2.41). Since $p(\nu)$ satisfies the KKT conditions associated with that QP problem, there exist Lagrange multipliers $\lambda(\nu) \in \mathbb{R}^m$ and $\mu(\nu)_i$, $i \in \mathcal{I}_{ac}\left(x^{(\nu)}\right)$, such that the Lagrange KKT condition $\nabla_x \mathcal{L}\left(x^{(\nu)}, \lambda^{(\nu)}, \mu^{(\nu)}\right) = 0$ holds. That is

$$-b^{(\nu)} = -\left(Bx^{(\nu)} - b\right) = -\sum_{i}^{m} \lambda_i^{(\nu)} c_i \quad - \sum_{i \in \mathcal{I}_{ac}\left(x^{(\nu)}\right)} \mu_i^{(\nu)} a_i. \tag{2.50}$$

If we set

$$\mu_i^{(\nu)} := 0 \quad , \quad i \in \{1, \ldots, p\} \setminus \mathcal{I}_{ac}\left(x^{(\nu)}\right), \tag{2.51}$$

then it is clear that $x^{(\nu)}$, $\lambda^{(\nu)}$, and $\mu^{(\nu)}$ satisfy the first KKT condition with respect to the original QP problem (2.36).

Since $x^{(\nu)}$ is feasible, the second and third KKT conditions also hold true.

We then check the fourth KKT condition in terms of the sign of the multiplier $\mu^{(\nu)}$ and proceed as follows:

- *for the case $\mu^{(\nu)} \geq 0 \quad , \quad i \in \mathcal{I}_{ac}\left(x^{(\nu)}\right)$, the fourth KKT condition holds true. Consequently, $x^{(\nu)}$ is a strict local minimum, since B is symmetric positive*

definite.

- *if* $\mu^{(\nu)} < 0$ *for some* $j \in \mathcal{I}_{ac}\left(x^{(\nu)}\right)$*, we remove the constraint corresponding to the negative multiplier from the active set. In other word, we remove an index* j *corresponding to one of the negative multipliers from the current active set and solve a new sub-problem of (2.41) for the new step. It is shown in ([30]) that this strategy produces a direction* p *in the subsequent iteration step that is feasible with respect to the dropped constraint.*

2.2.3 Newton Method

The Newton method for univariate case $g(x) = 0$

For simplicity, we assume the function $g(x) = 0$ has continuous second derivatives. Given the starting point x_0, the Newton method for finding the solution to the function $g(x) = 0$ is to compute an iterative scheme

$$x_{k+1} = x_k - \frac{g(x_k)}{g^{'}(x_k)},\ k = 1, 2, 3 \ldots . \tag{2.52}$$

Note that the iteration is defined only if $g^{'}(x_k) \neq 0$ at each step. When $g(x_k) = 0$, the iteration stops and the solution is achieved.

For a given iterate x_k, such that $g(x_k) \neq 0$, let $x = x_k + p$. We compute $g(x)$ as follows:

$$g(x) = g(x_k + p) \approx g(x_k) + pg^{'}(x_k). \tag{2.53}$$

We compute the value of p such that $g(x_k) + pg^{'}(x_k) = 0$.

The Newton method for multivariate case $g(x) = 0$

Let denote

$$g(x) = \begin{bmatrix} g_1(x) \\ g_2(x) \\ \vdots \\ g_n(x) \end{bmatrix}, \tag{2.54}$$

for the system $g(x) = 0$, i.e

$$g_i(x) = 0, \qquad i = 1, 2, \ldots, n. \tag{2.55}$$

We define the Jacobian matrix as follows:

$$\mathcal{J}(x) = \begin{bmatrix} \dfrac{\partial g_1(x)}{\partial x_j} \\ \dfrac{\partial g_2(x)}{\partial x_j} \\ \vdots \\ \dfrac{\partial g_n(x)}{\partial x_j} \end{bmatrix}. \tag{2.56}$$

The Newton iterative scheme is given by

$$x_{k+1} = x_k + \alpha d,$$

where we usually set α equal to one and d is the Newton direction, which can be computed from the first-order approximation of the Taylor series expansion. From the Taylor series approximation of g at the point x_k, we have:

$$g(x_{k+1}) \approx g(x_k) + \nabla \mathcal{J}(x_k) d. \tag{2.57}$$

We can solve for p when we set the right-hand side of the equation 2.57 to be zero, provided that the Jacobian matrix $\mathcal{J}(x_k)$ is non-singular. In general, the first-order Newton method is stated as follow

$$x_{k+1} = x_k - (\mathcal{J}(x_k))^{-1} g(x_k). \tag{2.58}$$

The Newton method for minimization problem

Let us consider a minimization problem of a convex function $f(x)$

$$\underset{x \in \mathbb{R}^n}{minimize} \qquad f(x). \tag{2.59}$$

The iterative scheme is

$$x_{k+1} = x_k + \alpha d, \tag{2.60}$$

where the value α is usually set equal to one and d is the Newton direction, which can be computed from the second-order approximation of the Taylor series

$$f(x_{k+1}) \approx t(x_k) = f(x_k) + \nabla f(x_k)(x_{k+1} - x_k) + \frac{1}{2}(x_{k+1} - x_k)^T H(x)(x_{k+1} - x_k), \tag{2.61}$$

where $H(x)$ is the Hessian of $f(x)$. To find the minimum of equation (2.61), we calculate

$$\nabla t(x_k) = \nabla f(x_k) + H(x)(x_{k+1} - x_k), \tag{2.62}$$

and set $\nabla t(x_k) = 0$. We get the following expression

$$\nabla f(x_k) + H(x)(x_{k+1} - x_k) = 0, \tag{2.63}$$

or

$$\nabla H(x)d = -f(x_k), \tag{2.64}$$

where d is the Newton direction and can be calculated from equation (2.64), provided that the Hessian matrix is positive definite.

Chapter 3

Modeling Problems

3.1 Modeling of Inorganic Aerosols

3.1.1 Chemical Equilibrium Formulation of the Problem

Consider a closed system of inorganic aerosol at constant temperature and pressure. Within this thermodynamic system, the aerosol particles exist in all phases: liquid (l), gas (g), and solid (s). The mass balance equation yields:

$$\hat{A}_l n_l + \hat{A}_g n_g + \hat{A}_s n_s = \hat{b}, \tag{3.1}$$

where $\hat{b}$ denotes the feed vector; $n_\alpha \in \mathbb{R}^{m_\alpha}$, and $\hat{A}_\alpha \in \mathbb{R}^{m_e \times m_\alpha}$ denote the concentration vector and coefficient matrix of the species for each phase set $\alpha = l, g, s$ respectively. The subscripts l, g, s denote the liquid, gas, and solid phases. We denote m_e as the number of chemical species in the system and m_α as the number of

species in phase set α. The Gibbs Free Energy of the system is defined:

$$G(n_l, n_g, n_s) = n_l^T \mu_l + n_g^T \mu_g + n_s^T \mu_s. \tag{3.2}$$

When the system reaches the equilibrium state, the Gibbs Free Energy of the system (3.2) reaches its minimum value. Thus, at equilibrium, we can solve the multi-phase and multi-reaction of a closed inorganic aerosol system by solving this minimization problem

$$\min \quad G(n_l, n_g, n_s) = n_l^T \mu_l + n_g^T \mu_g + n_s^T \mu_s, \tag{3.3a}$$

$$\text{s. t.} \quad n_l > 0, \quad n_g > 0, \quad n_s \geq 0, \tag{3.3b}$$

$$\hat{A}_l n_l + \hat{A}_g n_g + \hat{A}_s n_s = \hat{b}. \tag{3.3c}$$

The chemical potential vectors μ_α, for each phase $\alpha = g, l, s$, are defined as followed:

- For the gas phase:

$$\mu_g = \mu_g^0 + RT \log a_g, \tag{3.4}$$

where R is the universal gas constant that has a value $R = 8.31446\left(\frac{J}{molK}\right)$. T is the system temperature. μ_g^0 is the standard chemical potential vector of gas species at a pressure of 1 atm and the system temperature, and a_g is the activity vector which is defined as:

$$a_g = \frac{\hat{f}_g}{\hat{f}_{g,SS}} = \frac{\hat{f}_g}{1} = \hat{f}_g, \tag{3.5}$$

where $\hat{f}_{g,SS}$ is the fugacity of the gas species in its standard state. We assume that the gas in the system are ideal ($\hat{f}_{g,SS} = 1$). And $\hat{f}_g$ is the fugacity vector of the gas species and is given by

$$\hat{f}_g = y_b \hat{f}_g^0 = y_b \gamma_g P, \tag{3.6}$$

where $\hat{f}_g^0$ is the fugacity of pure component gas species evaluated at the system temperature and the total pressure P of the gas mixture, or by the fugacity coefficient γ_g.

- For the aqueous phase:

$$\mu_l = \mu_l^0 + RT \log a_l, \tag{3.7}$$

where 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 determined by an activity coefficient model.

- For the solid phase:

$$\mu_s = \mu_s^0, \tag{3.8}$$

where μ_s^0 is the standard chemical potential vector of the aqueous species at the system temperature and pressure.

Remark 3.1.1

Let us denote $\mathbb{R}_{++}$ be the strictly positive real numbers. Note that the chemical potential vector μ_l is also defined as the gradient of the Gibbs Free Energy of the aqueous phase as follows:

$$\mu_l = \nabla G_l(n_l), \tag{3.9}$$

where $G_l : \mathbb{R}^{m_l}_{++} \to \mathbb{R}_+$.

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

$$G_l(n_l) = n_l^T \mu_l, \tag{3.10}$$

and the Gibbs-Duhem equations:

$$\nabla^2 G_l(n_l) n_l = 0, \tag{3.11}$$

equivalently

$$(\nabla \mu_l)\, n_l = 0 \;\; or \;\; (\nabla \log a_l)\, n_l = 0.$$

The respective Hessian matrices are given by

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

3.2 Description of the Problem and Optimality Conditions

3.2.1 Optimality Conditions and the Karush-Kuhn-Tucker System

For general purposes, we assume that the aqueous and gas phases are present at equilibrium, the solution of the chemical equilibrium (3.3) is characterized by the Karush-Kuhn-Tucker (KKT) system of the first-order necessary optimality conditions:

$$\mu_l + \hat{A}_l^T \lambda_l = 0, \tag{3.12a}$$

$$\mu_g + \hat{A}_g^T \lambda_g = 0, \tag{3.12b}$$

$$\mu_s + \hat{A}_s^T \lambda \geq 0, \quad n_s \geq 0, \quad n_s^T(\mu_s + \hat{A}_s^T \lambda) = 0, \tag{3.12c}$$

$$\hat{A}_l n_l + \hat{A}_g n_g + \hat{A}_s n_s = \hat{b}. \tag{3.12d}$$

The KKT system (3.12) is referred to as the *stoichiometric form of the species* in the system at equilibrium. If we break down the aqueous species into component bases, we can formulate a computationally more relevant form, the *component stoichiometric form.*

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 gas, liquid, and solid phases of the corresponding index set $\mathcal{I}_g$,

$\mathcal{I}_l$, and $\mathcal{I}_s$, with $m_g := |\mathcal{I}_g|$, $m_l := |\mathcal{I}_l|$, and $m_s := |\mathcal{I}_s|$. The element-based formula matrices in (3.12d) are defined by $\hat{A}_\alpha = (\hat{a}_j)_{j\in\mathcal{I}_\alpha}$ for $\alpha = g, l, s$.

To ensure the feasibility of solid-liquid and gas-liquid equilibrium reactions in (3.3), we assume the following:

The species sets $\mathcal{I}_\alpha$, $\alpha = g, l, s$, in the system are assumed to follow that all the gas and solid species in the system can be generated as a linear combination of the aqueous species

$$\text{range}(\hat{A}_l, \hat{A}_g, \hat{A}_s) = \text{range}(\hat{A}_l). \tag{3.13}$$

In other words, the number of the aqueous species is larger than the number of the elements ($m_l > m_e$).

Let m_c ($\leq m_e$) be the rank of $\hat{A}_l$. We denote $\mathcal{I}_c$ to be the set m_c of components where the corresponding formula vectors $\hat{a}_i$) are linear independent. Similarly, we denote m_n and $\mathcal{I}_n$ for noncomponents. Note that $\mathcal{I}_l = \mathcal{I}_c \cup \mathcal{I}_n$. 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

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

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

$$\mathcal{X}_j \leftrightarrows \sum_{i\in\mathcal{I}_c} a^\alpha_{ij}\mathcal{X}_i, \quad \forall j \in \mathcal{I}_\alpha, \qquad \text{for } \alpha = c, n, g, s. \tag{3.14}$$

where $\mathcal{X}$ denotes species and their components, and a^α_{ij} are stoichiometric coefficients. The corresponding *canonical equilibrium-constant* vector $k_\alpha = (k^\alpha_j)_{j\in\mathcal{I}_\alpha}$ is defined by

$$-RT\log k_\alpha := A_\alpha^T\mu_c^0 - \mu_\alpha^0, \qquad \text{for } \alpha = c, n, s, g \tag{3.15}$$

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.

Remark 3.2.1

The mass balance equations in (3.1) can be replaced by the component balance equations

$$n_c + A_n n_n + A_g n_g + A_s n_s = b. \tag{3.16}$$

Proof. To derive 3.16, let us start with the mass balance equation in (3.1)

$$\begin{aligned}
\hat{A}_l n_l + \hat{A}_g n_g + \hat{A}_s n_s &= \hat{b} \\
\hat{A}_c^{-1}\left(\hat{A}_l n_l + \hat{A}_g n_g + \hat{A}_s n_s\right) &= \hat{A}_c^{-1}\hat{b} && \text{multiply } \hat{A}_c^{-1} \text{ both side} \\
\hat{A}_c^{-1}\left(\hat{A}_c n_c + \hat{A}_n n_n + \hat{A}_g n_g + \hat{A}_s n_s\right) &= \hat{A}_c^{-1}\hat{b} && \text{since } \hat{A}_l n_l = \hat{A}_c n_c + \hat{A}_n n_n \\
n_c + A_n n_n + A_g n_g + A_s n_s &= b && \text{since } A_\alpha := \hat{A}_c^{-1}\hat{A}_\alpha \text{ and } b = \hat{A}_c^{-1}\hat{b}
\end{aligned}$$

□

Remark 3.2.2

The Gibbs Free Energy in the chemical equilibrium equation (3.2) can also be reformulated by replacing the chemical potentials in terms of activities and equilibrium constants via (3.4),(3.7),(3.8), (3.15), and (3.16):

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

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

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

The problem (3.3) can be written in the *adimensional canonical stoichiometric form* (dropping the tilde in the notation):

$$\min \qquad G(n_l, n_g, n_s) = n_c^T \log a_c + n_n^T (\log a_n + \log k_n) \tag{3.17a}$$
$$+ n_g^T (\log a_g + \log k_g) + n_s^T \log k_s, \tag{3.17b}$$
$$\text{s. t.} \qquad n_l = \begin{pmatrix} n_c \\ n_n \end{pmatrix} > 0, \quad n_g > 0, \quad n_s \geq 0, \tag{3.17c}$$
$$n_c + A_n n_n + A_g n_g + A_s n_s = b. \tag{3.17d}$$

The KKT system of (3.17) can be written in the *primal-dual canonical stoichiometric form*:

$$\log a_c + \lambda = 0, \tag{3.18}$$
$$\log a_n + A_n^T \lambda = -\log k_n, \tag{3.19}$$
$$\log a_g + A_g^T \lambda = -\log k_g, \tag{3.20}$$
$$\log k_s + A_s^T \lambda \geq 0, \quad n_s \geq 0, \tag{3.21}$$
$$n_s^T (\log k_s + A_s^T \lambda) = 0, \tag{3.22}$$
$$n_c + A_n n_n + A_g n_g + A_s n_s = b. \tag{3.23}$$

Remark 3.2.3

The above KKT system furnishes the mass action laws (3.18)-(3.22) in addition to the mass balance constraints (3.23). 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 (3.18)-(3.22) are linear with respect to the dual variable λ.

3.2.2 Chemical Equilibrium Problem at Fixed Relative Humidity

In atmospheric aerosol thermodynamic calculations, the ambient relative humidity (RH) is usually treated as a known constant.

Definition 3.2.1 **(Relative humidity)**

Relative humidity (RH) is the ratio of the partial pressure of water vapor p_w to the equilibrium vapor pressure of water p_w^0 at the same temperature.

$$RH = \frac{p_w}{p_w^0}, \tag{3.24}$$

where RH is expressed in the 0 *to* 1 *scale.*

Remark 3.2.4

From the definition of $\log a_{H_2O(g)}$ *in (3.5) and* $\log k_{H_2O(g)}$ *in (3.15), it follows that*

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

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

$$n_{H_2O(total)} = n_{H_2O(g)} + n_{H_2O(pm)}, \tag{3.25}$$

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

The total feed vector b is split into the non-water quantity $\bar{b}$ and the water quantity as follows:

$$b = \bar{b} + n_{\mathrm{H_2O(total)}} a_{\mathrm{H_2O}}, \tag{3.26}$$

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 (3.25) and (3.26) 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 (3.17) 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 (3.17) 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, it can be disregarded. The chemical equilibrium problem gives

$$
\begin{aligned}
\min \quad & G(n_l, \bar{n}_g, n_s, n_{\mathrm{H_2O(pm)}}) = n_c^T \log a_c + n_n^T (\log a_n + \log k_n) && (3.27\mathrm{a}) \\
& + \bar{n}_g^T (\log \bar{a}_g + \log \bar{k}_g) + n_s^T \log k_s - n_{\mathrm{H_2O(pm)}} \log \mathrm{RH}, && (3.27\mathrm{b}) \\
\text{s. t.} \quad & n_l = \begin{pmatrix} n_c \\ n_n \end{pmatrix} > 0, \quad n_g > 0, \quad n_s \geq 0, \quad n_{\mathrm{H_2O(pm)}} > 0 && (3.27\mathrm{c}) \\
& n_c + A_n n_n + \bar{A}_g \bar{n}_g - n_{\mathrm{H_2O(pm)}} a_{\mathrm{H_2O}} + A_s n_s = \bar{b}. && (3.27\mathrm{d})
\end{aligned}
$$

The KKT system for the chemical equilibrium problem (3.27) can be written in the primal-dual canonical stoichiometric form:

$$\log a_c + \lambda = 0, \tag{3.28}$$

$$\log a_n + A_n^T \lambda = -\log k_n, \tag{3.29}$$

$$\log \bar{a}_g + \bar{A}_g^T \lambda = -\log \bar{k}_g, \tag{3.30}$$

$$\log \mathrm{RH} + a_{\mathrm{H_2O}}^T \lambda = 0, \tag{3.31}$$

$$\log k_s + A_s^T \lambda \geq 0, \quad n_s \geq 0, \tag{3.32}$$

$$n_s^T (\log k_s + A_s^T \lambda) = 0, \tag{3.33}$$

$$n_c + A_n n_n + \bar{A}_g \bar{n}_g - n_{\mathrm{H_2O(pm)}} a_{\mathrm{H_2O}} + A_s n_s = \bar{b}. \tag{3.34}$$

Remark 3.2.5

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. $n_{H_2O(pm)} = n_{l,w}$, *by neglecting the part of* $n_{H_2O(pm)}$ *that is dissociated into electrolytes via*

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

The aqueous water content $n_{l,w}$ *is usually predicted using an empirical relationship (Zdanovskii, Robinson, and Stokes equation,* ZSR *[34]). The limitations of this empirical method are the additional needs of the saturated molarities of electrolytes according to the relative humidity. For this reason, there are thermodynamic inconsistency within the specific activity coefficient model that is used to predict the activity of the aqueous phase.*

For simplification purpose, 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 (3.28)-(3.34), the primal variables $n_{\mathrm{H_2O(pm)}}$ and n_s occur only in the mass balance constraints (3.34). They can be viewed respectively as the multipliers of the saturation constraints (3.31) and (3.32) on the dual variable λ, thus will be eliminated by applying the so-called null-space method for the solution of (3.28)-(3.34). This observation is the key for the development of the primal-dual active set algorithm detailed in the next section.

Chapter 4

Methods and Algorithm

4.1 Phase Stability Criterion and Active Set

A primal-dual solution of the KKT system (3.18)-(3.23) or (3.28)-(3.34), generally non-unique, is called a KKT point. Also, this solution may not be a local minimizer of the Gibbs Free Energy. It is necessary 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.

Denote $(n_l^\dagger, n_g^\dagger, n_s^\dagger, \lambda^\dagger)$ to be the a KKT point of (3.18)-(3.23) or (3.28)-(3.34). Let

$$\bar{\mathcal{I}}_s^\dagger := \{i \in \mathcal{I}_s : n_{s,i}^\dagger > 0\}, \tag{4.1}$$

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 to hold:

$$p^T H p > 0, \qquad \text{for all nonzero vector } p \text{ such that } \bar{A}p = 0, \tag{4.2}$$

where $H = \nabla^2_{n_l,n_g,n_s} G(n_l^\dagger, n_g^\dagger, n_s^\dagger)$ is the Hessian matrix of the Gibbs Free Energy of the system, $\bar{A} = [A_l, A_g, \bar{A}_s]$ and $\bar{A}_s := (a_i^s)_{i \in \bar{\mathcal{I}}_s^\dagger}$.

Moreover, the following assumptions are made for the system:

(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 (K. Denbig [12]), 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

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

The above constraints are extracted from the complementary slackness conditions (3.22) or (3.33).

(H2) The formula vectors of solids that actually precipitated in the system $(a_i^s)_{i \in \bar{\mathcal{I}}_s^\dagger}$ were assumed to be linearly independent (*linear independent constraints qualification*, see also A. F. Izmailov and M. V. Solodov [17] 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 (3.32) (3.33)), 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).

4.2 Inertia Theory

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 general 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 (4.2) 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 4.2.1

Under assumptions (H1) and (H2) and if (4.2) is satisfied, the KKT matrix K is invertible.

Proof. Based on an inertia result of Gould [16], we have

$$\text{inertia}(K) = \text{inertia}(Z_{\bar{A}}^T H Z_{\bar{A}}) + (m_c, m_c, 0), \tag{4.3}$$

where $Z_{\bar{A}}$ is a null-space matrix for $\bar{A}$. Then (4.2) implies

$$\text{inertia}(K) = (m_l + m_g + \bar{m}_s, m_c, 0). \tag{4.4}$$

The matrix K is thus invertible. $\square$

Solving (3.18)-(3.23) or (3.28)-(3.34) may not be easy, it is mainly because of the combinatorial aspect of the KKT system, or more precisely by the complementary slackness conditions (3.22) or (3.33). The problem is not only to determine the concentrations but also to guess the *optimal active set* of solids (in the "dual" sense)

$$\bar{\mathcal{I}}_s^\dagger := \{\, j \in \mathcal{I}_s : \log k_{s,j} + a_{s,j}^T \lambda^\dagger = 0 \,\}. \tag{4.5}$$

Under assumption (H3) that the *strictly complementary slackness* condition holds, $\bar{\mathcal{I}}_s^\dagger$ is equal to the "primal" set defined in (4.1), *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, or the complementary solid set of $\bar{\mathcal{I}}_s^\dagger$, is denoted as follows:

$$\tilde{\mathcal{I}}_s^\dagger := \mathcal{I}_s \setminus \bar{\mathcal{I}}_s^\dagger = \{\, j \in \mathcal{I}_s : \log k_{s,j} + a_{s,j}^T \lambda^\dagger > 0 \,\}. \tag{4.6}$$

It 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 (4.5), the KKT system (3.18)-(3.23) or (3.28)-(3.34) can be transformed into a system of nonlinear equations, which is much more computationally tractable. Let us define

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

The *exact solution* of the chemical equilibrium problem (3.27) can be computed from the KKT conditions as follow:

$$\log a_c + \lambda = 0, \tag{4.7}$$

$$\log a_n + A_n^T\lambda = -\log k_n, \tag{4.8}$$

$$\log a_g + A_g^T\lambda = -\log k_g, \tag{4.9}$$

$$\log \mathrm{RH} + a_{\mathrm{H_2O}}^T\lambda = 0, \tag{4.10}$$

$$\log \bar{k}_s + \bar{A}_s^T\lambda = 0, \quad \bar{n}_s > 0, \tag{4.11}$$

$$\log \tilde{k}_s + \tilde{A}_s^T\lambda > 0, \quad \tilde{n}_s = 0, \tag{4.12}$$

$$n_c + A_n n_n + A_g n_g - n_{\mathrm{H_2O(pm)}} a_{\mathrm{H_2O}} + \bar{A}_s\bar{n}_s = \bar{b}, \tag{4.13}$$

where the complementary slackness conditions (3.32) and (3.33) are split into the equalities (4.11) and the strict inequalities (4.12), according to the optimal active and inactive sets of solid phases, $\bar{\mathcal{I}}_s^\dagger$ and $\tilde{\mathcal{I}}_s^\dagger$, respectively.

Let us simplify the notations by denoting

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

The "dual" saturation constraints (4.10) and (4.11) are combined to form the dual linear equality constraint

$$\bar{A}_\lambda \lambda = \bar{b}_\lambda. \tag{4.14}$$

The feasibility of (4.14) 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 (4.14) 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 (4.14). The primal variables $n_{\mathrm{H_2O(pm)}}$ and $\bar{n}_s$ are viewed as the multiplier of the combined dual equality constraint (4.14). Replacing λ by the reduced variable η and projecting the KKT system (4.7)-(4.13) 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*:

$$\log a_c + Z_{\bar{A}_\lambda} \eta = -\lambda^*, \tag{4.15}$$

$$\log a_n + A_n^T Z_{\bar{A}_\lambda} \eta = -\log k_n - A_n^T \lambda^*, \tag{4.16}$$

$$\log a_g + A_g^T Z_{\bar{A}_\lambda} \eta = -\log k_g - A_g^T \lambda^*, \tag{4.17}$$

$$Z_{\bar{A}_\lambda}^T n_c + Z_{\bar{A}_\lambda}^T A_n n_n + Z_{\bar{A}_\lambda}^T A_g n_g = Z_{\bar{A}_\lambda}^T \bar{b}. \tag{4.18}$$

Once the solution (n_c, n_n, n_g, η) of the reduced system (4.15)-(4.18) is known, one can compute the primal variables $n_{\mathrm{H_2O(pm)}} > 0$ and $\bar{n}_s > 0$, from the mass-balance equations (4.13) via

$$\begin{pmatrix} n_{\mathrm{H_2O(pm)}} \\ \bar{n}_s \end{pmatrix} = \left(\bar{A}_\lambda^T\right)^{-1} \left(\bar{b} - n_c - A_n n_n - A_g n_g\right), \tag{4.19}$$

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.

4.3 Primal-Dual Active Set Method

In order to solve (3.18)-(3.23) or (3.28)-(3.34), 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 (4.5) as follow

$$\bar{\mathcal{I}}_s := \{\, j \in \mathcal{I}_s : \log k_{s,j} + a_{s,j}^T \lambda = 0 \,\}, \tag{4.20}$$

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 (3.28)-(3.34). By the definition (4.20), $\bar{\mathcal{I}}_s$ is the set of the linear

inequalities (3.32) 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 (3.32) being inactive at λ, *i.e.*,

$$\tilde{\mathcal{I}}_s := \mathcal{I}_s \setminus \bar{\mathcal{I}}_s = \{\, j \in \mathcal{I}_s : \log k_{s,j} + a_{s,j}^T \lambda > 0 \,\}. \tag{4.21}$$

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.*,

$$\log k_{s,j} + a_{s,j}^T \lambda = 0, \quad \forall j \in \bar{\mathcal{I}}_s, \tag{4.22}$$

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

$$\log k_{s,j} + a_{s,j}^T \lambda \geq 0, \quad \forall j \in \tilde{\mathcal{I}}_s. \tag{4.23}$$

The principle of the algorithm is the following. The dual feasibility condition of inequalities (4.23) 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 (4.22) 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 (3.28)-(3.34) 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 (4.15)-(4.18) with the particular solution λ^* of (4.14) 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 (4.23). 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 (3.28)-(3.34) 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 (4.19). Since $\bar{n}_s$ is viewed as the Lagrange *multipliers* of the dual active constraints (4.22), 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.

For the moment, let us disregard the fact that $\bar{n}_s$ must remain non-negative, and simply apply the Newton method to the reduced KKT system to compute a displacement, denoted by $(p_{n_l}, p_{n_g}, p_\lambda)$, in (n_l, n_g, λ). We set $p_\lambda = Z_{\bar{A}_\lambda} p_{\boldsymbol{\eta}}$ for a certain $\boldsymbol{\eta}$, and λ must satisfy (4.22). This reduced KKT system, projected on $\bar{\mathcal{I}}_s$, is the following symmetric indefinite system:

$$\begin{pmatrix} H_l & 0 & A_{zl}^T \\ 0 & H_g & A_{zg}^T \\ A_{zl} & A_{zg} & 0 \end{pmatrix} \begin{pmatrix} p_l \\ p_g \\ p_{\boldsymbol{\eta}} \end{pmatrix} = \begin{pmatrix} b_l \\ b_g \\ b_{\boldsymbol{\eta}} \end{pmatrix}, \tag{4.24}$$

where

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

and

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

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

$$\tilde{\mathcal{I}}_g := \{\, j \in \mathcal{I}_g : \; Z_{\bar{A}_\lambda}^T a_j^g = 0 \,\}, \tag{4.25}$$

$$\bar{\mathcal{I}}_g := \mathcal{I}_g \setminus \tilde{\mathcal{I}}_g, \quad \bar{m}_g := |\bar{\mathcal{I}}_g|, \tag{4.26}$$

$$\bar{A}_g := (a_j^g)_{j \in \bar{\mathcal{I}}_g}, \quad \bar{A}_{zg} := Z_{\bar{A}_\lambda}^T \bar{A}_g. \tag{4.27}$$

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

$$A_{zg} P = (\bar{A}_{zg}, 0), \tag{4.28}$$

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 (3.28)-(3.34) is then obtained by

$$n_l^+ = n_l + \alpha\, p_l, \tag{4.29a}$$

$$n_g^+ = n_g + \alpha\, p_g, \tag{4.29b}$$

$$\lambda^+ = \lambda + \alpha\, p_\lambda. \tag{4.29c}$$

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.* [14]. The maximum feasible steplength $\bar{\alpha}$ is computed by using a ratio test

$$\bar{\alpha} = \min \left\{ \frac{\log k_{s,j} + a_{s,j}^T \lambda}{-a_{s,j}^T p_\lambda} \;:\; a_{s,j}^T p_\lambda < 0,\, j \notin \bar{\mathcal{I}}_s \right\}, \tag{4.30}$$

so that the new estimate λ^+ stays feasible with respect to the inequality constraints (4.23), *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 (4.22).

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 (4.14), 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

$$\mathcal{P}^a \neq \emptyset \quad \text{implies} \quad \bar{\mathcal{I}}_s^a \neq \emptyset. \tag{4.31}$$

The implication of (4.31) 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 (4.14), the associated matrix $\bar{A}_s^+$ must have full rank, so does $\bar{A}_\lambda^+$, see also [15].

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 (4.15)-(4.18) 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

$$\mathcal{P}^d \neq \emptyset \quad \text{implies} \quad \bar{\mathcal{I}}_s^d \neq \emptyset. \tag{4.32}$$

The implication of (4.32) 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 (3.28)-(3.34) is reached, and the algorithm stops. This active set/Newton algorithm is summarized in the next section.

4.4 Active Set Method algorithms

The principal features of the algorithm can be summarized as following:

- The algorithm applies Newton 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* is used 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 so 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-negative characteristic 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).

- To avoid the negative values and inaccurate 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. After that, it converges quadratically to the minimum of the Gibbs Free Energy.

Remark 4.4.1

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

Table 4.1: 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 (4.24);

Step 2. Compute the steplength $\bar{\alpha}$ with (4.30);

Step 3. Update n_l^+, n_g^+ and $\boldsymbol{\lambda}^+$ with (4.29);

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 $n_{\mathrm{H}_2 0}^+$ with (4.19):

- If $\bar{n}_s^+, n_{\mathrm{H}_2 0}^+ \geq 0$, 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)

4.5 Computation of Newton Direction

Consider the linear KKT system (4.24) 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 4.5.1

The condition (4.4) is equivalent to

$$\mathit{inertia}(\bar{K}) = (m_l + m_g, m_{zc}, 0), \tag{4.33}$$

where

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

Proof. The proof is a direct consequence of (4.3) 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 matrices with

$$Q_g \in \mathbb{R}^{m_{zc}\times\bar{m}_g}, \quad \tilde{Q}_g \in \mathbb{R}^{m_{zc}\times(m_{zc}-\bar{m}_g)}, \quad Q_l \in \mathbb{R}^{m_l\times m_{zc}}, \quad \tilde{Q}_l \in \mathbb{R}^{m_l\times(m_l-m_{zc})},$$

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 4.5.1

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

$$Z_{A_{zl}}^T H_l Z_{A_{zl}} > 0, \tag{4.34}$$

$$\tilde{Z}_{A_{zl}}^T H_l \tilde{Z}_{A_{zl}} + R_g^{-T}\bar{H}_g R_g^{-1} > 0, \tag{4.35}$$

where $\tilde{Z}_{A_{zl}} = Q_l R_l^{-T} Q_g$ *and* $\bar{H}_g = diag(1/n_j^g)_{j\in\bar{\mathcal{I}}_g}$. *Conditions (4.34) and (4.35) are sufficient conditions for the system (4.24) to be solvable.*

Proof. The following proof is a constructive proof that also emphasize the solution method of (4.24) and the computation of the Newton direction.

The range-space method is applied to eliminate p_g from (4.24), giving

$$\begin{pmatrix} H_l & A_{zl}^T \\ A_{zl} & -S_g \end{pmatrix} \begin{pmatrix} p_l \\ p_\eta \end{pmatrix} = \begin{pmatrix} b_l \\ c_\eta \end{pmatrix}, \tag{4.36}$$

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 (4.36) is solved, p_g can be easily obtained from p_η via

$$p_g = H_g^{-1}(b_g - A_{zg}^T p_\eta). \tag{4.37}$$

Let

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

Lemma 4.5.2

Relationship (4.33) is equivalent to

$$\textit{inertia}(\tilde{K}) = (m_l, m_{zc}, 0). \tag{4.38}$$

Proof. The inertia relation, see for instance [16], 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 (4.36). It follows from (4.28) 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

$$\text{inertia}(S_g) = \begin{cases} (\bar{m}_g, 0, m_{zc} - \bar{m}_g), & \text{if } m_{zc} \geq \bar{m}_g, \\ (m_{zc}, 0, 0), & \text{otherwise.} \end{cases} \tag{4.39}$$

The condition (4.39) 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 (3.11).

For the solution of the system (4.36), 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 4.5.3

By defining $p_{\eta_1} = Q_g^T p_\eta$ and $p_{\eta_2} = \tilde{Q}_g^T p_\eta$, the linear system (4.36) is equivalent to solving

$$\begin{pmatrix} H_l + S_l & A_{zl}^T \tilde{Q}_g \\ \tilde{Q}_g^T A_{zl} & 0 \end{pmatrix} \begin{pmatrix} p_l \\ p_{\eta_2} \end{pmatrix} = \begin{pmatrix} c_l \\ \tilde{Q}_g^T c_\eta \end{pmatrix}, \tag{4.40}$$

where

$$c_l = b_l + A_{zl}^T Q_g R_g^{-T} \bar{H}_g R_g^{-1} Q_g^T c_\eta, \tag{4.41}$$

$$S_l = A_{zl}^T Q_g R_g^{-T} \bar{H}_g R_g^{-1} Q_g^T A_{zl}. \tag{4.42}$$

Proof. Let

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

Hence

$$V^T \tilde{K} V = \begin{pmatrix} H_l & A_{zl}^T Q \\ Q^T A_{zl} & -Q^T S_g Q \end{pmatrix} = \begin{pmatrix} H_l & A_{zl}^T Q_g & A_{zl}^T \tilde{Q}_g \\ Q_g^T A_{zl} & -R_g \bar{H}_g^{-1} R_g^T & 0 \\ \tilde{Q}_g^T A_{zl} & 0 & 0 \end{pmatrix}. \tag{4.43}$$

The system (4.36) is multiplied by V^T from the left on both sides and (4.43) 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:

$$\begin{pmatrix} -R_g \bar{H}_g^{-1} R_g^T & Q_g^T A_{zl} & 0 \\ A_{zl}^T Q_g & H_l & A_{zl}^T \tilde{Q}_g \\ 0 & \tilde{Q}_g^T A_{zl} & 0 \end{pmatrix} \begin{pmatrix} p_{\eta_1} \\ p_l \\ p_{\eta_2} \end{pmatrix} = \begin{pmatrix} Q_g^T c_\eta \\ b_l \\ \tilde{Q}_g^T c_\eta \end{pmatrix}. \tag{4.44}$$

Since $-R_g \bar{H}_g^{-1} R_g^T$, the $(1,1)$ block matrix system, is non-singular, the range-space method is applied to eliminate p_{η_1} from (4.44). Thus, equations (4.40) - (4.42) are achieved. $\square$

Note that, with the definitions in Lemma 4.5.3, p_η is obtained from

$$p_\eta = (Q_g \;\; \tilde{Q}_g) \begin{pmatrix} p_{\eta_1} \\ p_{\eta_2} \end{pmatrix} = Q_g p_{\eta_1} + \tilde{Q}_g p_{\eta_2}. \tag{4.45}$$

Once (4.40) is solved, the direction p_{η_1} can easily be obtained from p_l via

$$p_{\eta_1} = -R_g^{-T}\bar{H}_g R_g^{-1} Q_g^T (c_\eta - A_{zl} p_l). \tag{4.46}$$

Then let us define the matrix $\ddot{K}$ of the linear system (4.40) by

$$\ddot{K} = \begin{pmatrix} H_l + S_l & A_{zl}^T \tilde{Q}_g \\ \tilde{Q}_g^T A_{zl} & 0 \end{pmatrix}. \tag{4.47}$$

A stability analysis for the solvability of the system (4.40) is performed in the next lemma.

Lemma 4.5.4

The condition (4.38) is equivalent to the condition

$$Z_l^T (H_l + S_l) Z_l > 0, \tag{4.48}$$

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 (4.33) or (4.48), the linear system (4.40) is solvable.

Proof. Relationship (4.3) 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 (4.38) implies that

$$\text{inertia}(\ddot{K}) = (m_l, m_{zc} - \bar{m}_g, 0). \tag{4.49}$$

The Schur complement S_l in (4.47) is positive semidefinite. Since $\tilde{Q}_g^T A_{zl} \in \mathbb{R}^{(m_{zc}-\bar{m}_g)\times m_l}$ in (4.47) is of full rank $m_{zc} - \bar{m}_g$ by (4.3), 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 (4.49) 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 (4.48). Thus, the desired conclusion is achieved. □

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 (4.48), 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 (4.42), 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, (4.48) is equivalent to require that the conditions (4.34) and (4.35) hold and the conclusion of the theorem holds. □

Remark 4.5.1

Note that the condition (4.34), i.e., $Z_{A_{zl}}^T H_l Z_{A_{zl}} > 0$, *implies that*

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

That is, if $\bar{m}_g = 0$, the condition (4.34) alone implies that K has the desire inertia (4.4)*. For $\bar{m}_g > 0$, the additional condition (4.35) is required.*

From the solvability condition (4.48) that is derived from the above analysis on the phase stability, the system (4.40) 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 (4.2) is enforced by controlling H_l at each iteration. In other words, we replace H_l by a modification $\tilde{H}_l$ so that $Z_l^T(\tilde{H}_l + S_l)Z_l$ is sufficiently positive definite while $Z_l^T(H_l + S_l)Z_l$ is not sufficiently positive definite. Various methods for modifying H_l may be found in [30] for instance. Note that

$$Z_l^T(\tilde{H}_l + S_l)Z_l = Z_l^T \tilde{H}_l Z_l + \begin{pmatrix} 0 & 0 \\ 0 & R_g^{-T} \bar{H}_g R_g^{-1} \end{pmatrix}. \tag{4.50}$$

The system (4.40) or, more precisely, the system

$$\begin{pmatrix} \tilde{H}_l + S_l & A_{zl}^T \tilde{Q}_g \\ \tilde{Q}_g^T A_{zl} & 0 \end{pmatrix} \begin{pmatrix} p_l \\ p_{\eta_2} \end{pmatrix} = \begin{pmatrix} c_l \\ \tilde{Q}_g^T c_\eta \end{pmatrix} \tag{4.51}$$

has the solution given by:

$$p_l = Z_l(Z_l^T(\tilde{H}_l + S_l)Z_l)^{-1}Z_l^T\left(c_l - (\tilde{H}_l + S_l)p_l^*\right) + p_l^*, \tag{4.52}$$

$$p_{\eta_2} = \left(A_{zl}^T\tilde{Q}_g\right)^{-1}\left(c_l - (\tilde{H}_l + S_l)p_l\right), \tag{4.53}$$

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

$$\left(A_{zl}^T\tilde{Q}_g\right)^{-1} = \tilde{Q}_g^T(A_{zl}^{-1})^T, \tag{4.54}$$

and p_l^* is a particular solution of the second equation of (4.51), given by

$$p_l^* = A_{zl}^{-1}c_\eta. \tag{4.55}$$

In summary, for the solution of (4.24), the combination of Schur complements and null-space methods permits to solve successively (4.51) to obtain p_l and $p_{\boldsymbol{\eta}_2}$. Then p_{η_1} is obtained from (4.46), giving p_η with (4.45) and $p_\lambda = Z_{\bar{A}_\lambda}p_\eta$. Finally p_g is obtained with (4.37) to increment all the variables (n_l, n_g, λ) for next iteration.

Chapter 5

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.

The data input parameters for the model are physical parameters as temperature, relative humidity, pressure, and the feed vector $\bar{b}$, as well as stoichiometry matrix $A = [A_l, A_g, A_s]$.

The Gibbs Free Energy and the activity coefficients are computed with the *Extended UNIQUAC* model [35].

Two numerical examples in the multi-stage growth of atmospheric aerosols are documented 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 2.1.

Table 5.1: 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 describes the reactions with phase changes which may lead to the formation 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:

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

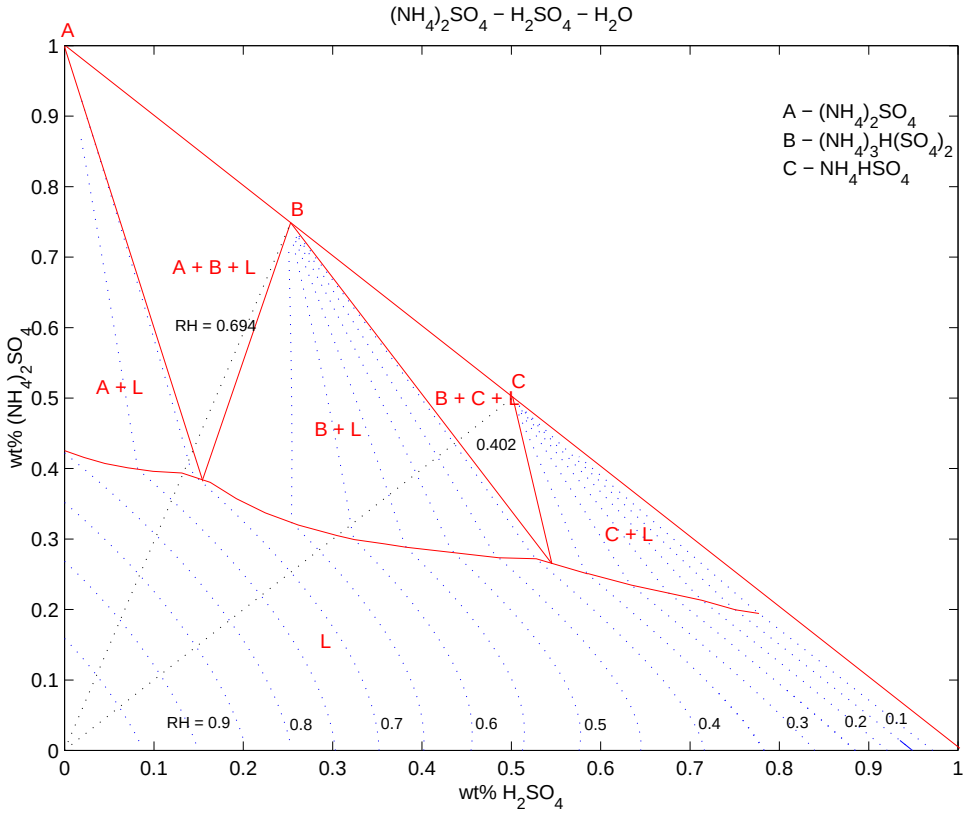
The vapor-liquid equilibrium reaction expresses the changes between water (l/aq = liquid/aqueous phase) and water vapor (g=gas phase), in which the relative humidity is a given constant; the speciation equilibria describe the interactions in the aqueous phase, while the solid-liquid equilibria are the reactions giving birth to a solid phase. In Figure 5.1, 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 5.2, the evolution of the aerosol particle with the feed vector $\bar{b}$ corresponding to three solids A, B, and C in Figure 5.1, 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 5.3 shows the typical Newton iteration in UHAERO.

5.2 Urban and Remote Continental Aerosols

The second example is two types of aerosols: urban and remote continental [28], 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

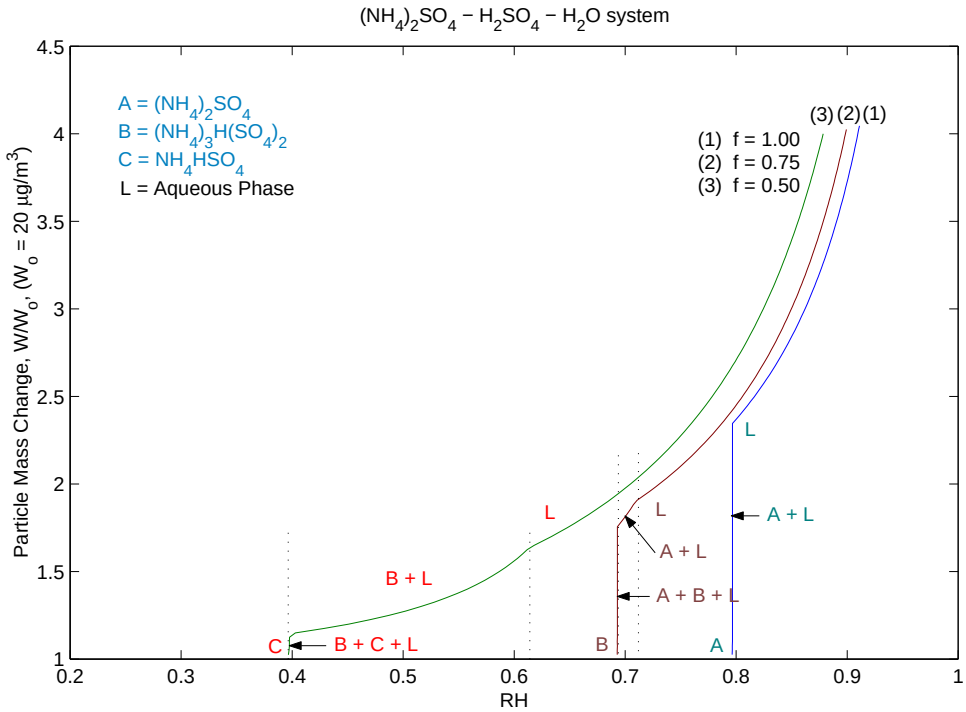
Figure 5.1: Modeling of a sulfate aerosol. Reconstruction of the phase diagram at 25^oC with tracking of the presence of each solid phases. For each region of space the existing phases at equilibrium are represented.



the chemical components of the system are given in Table 5.2.

In Figures 5.4 and 5.5, the mass ratios of inorganic components and water in typical urban and remote continental aerosols are given as a function of the relative humidity. Figures 5.4 and 5.5 illustrate clearly that the phase transitions are accurately tracked without any *a priori* knowledge of the existing phases. In Figures 5.6 and 5.7, 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

Figure 5.2: 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).



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

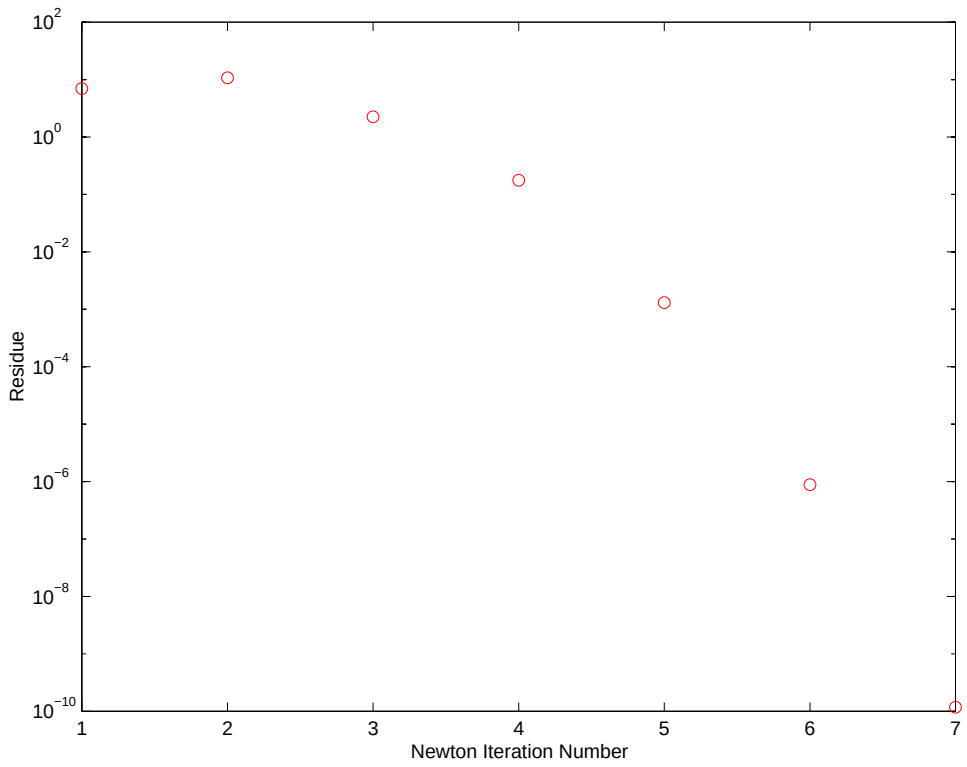


Table 5.2: Chemical equilibrium reactions in sulfate/nitrate system.

- 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:

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

Figure 5.4: 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 $NH_4^+ = 3.400\mu g/m^3$.

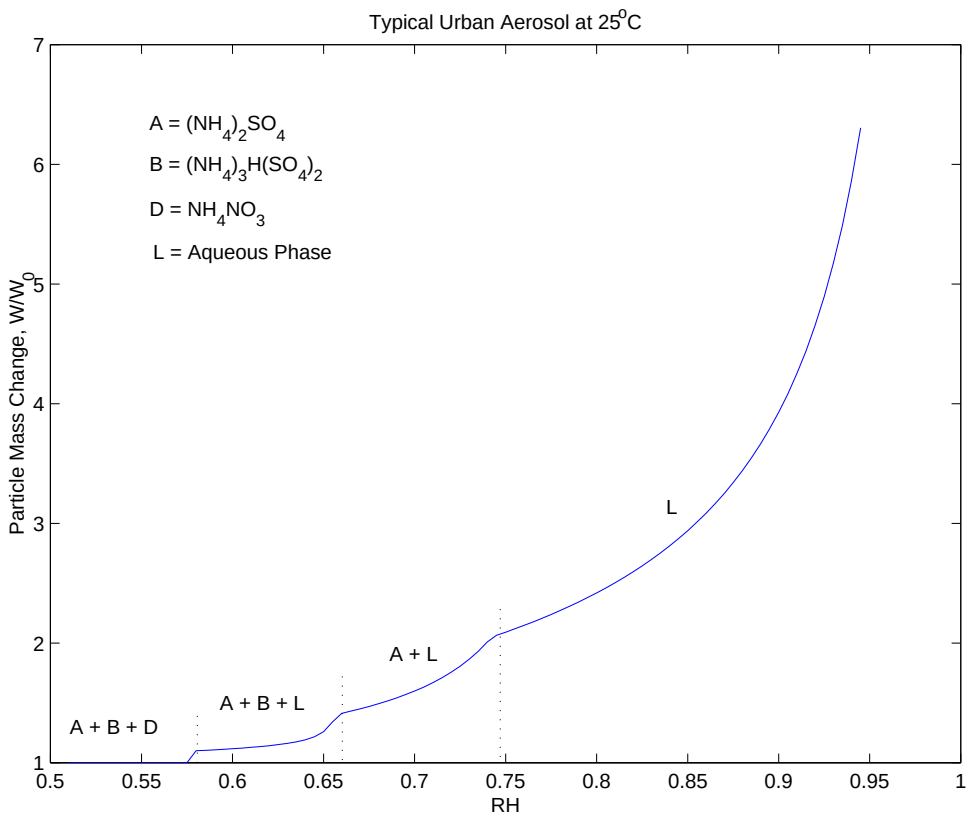


Figure 5.5: Deliquescence curve for sulfate/nitrate aerosol. Total $SO_4^{2-} = 11.270\mu g/m^3$, total $NO_3^- = 0.145\mu g/m^3$ and total $NH_4^+ = 4.250\mu g/m^3$.

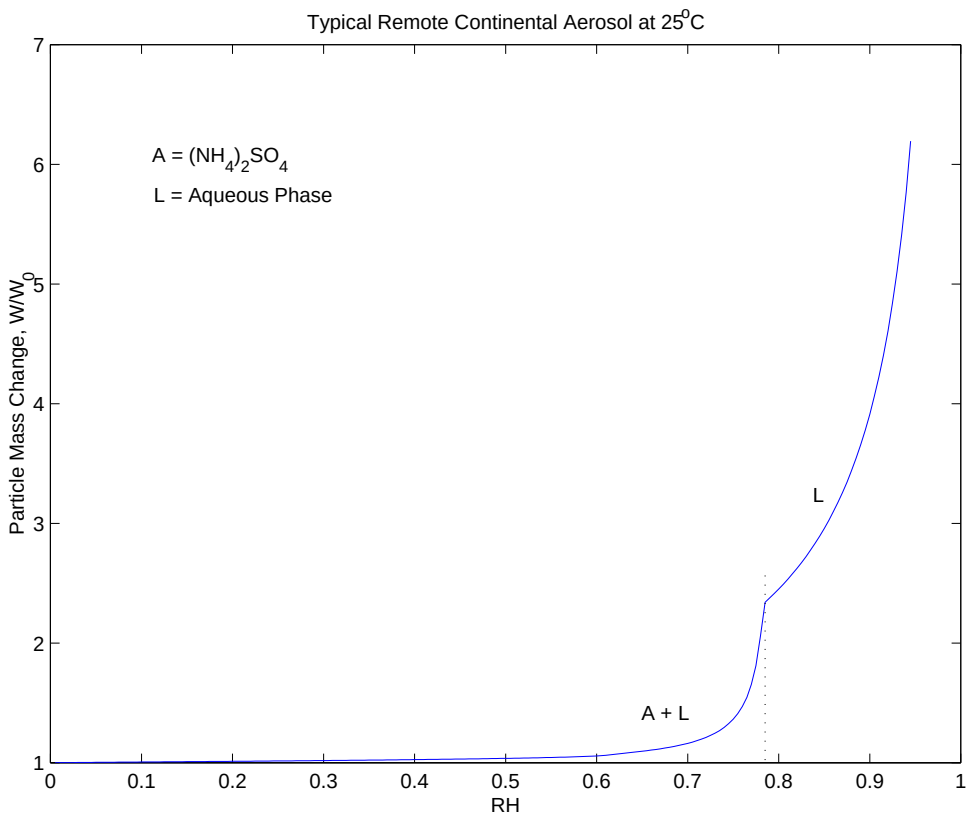


Figure 5.6: Evolution of solid content of aerosol in Figure 5.4. $W_0 = 14.496 \mu g/m^3$.

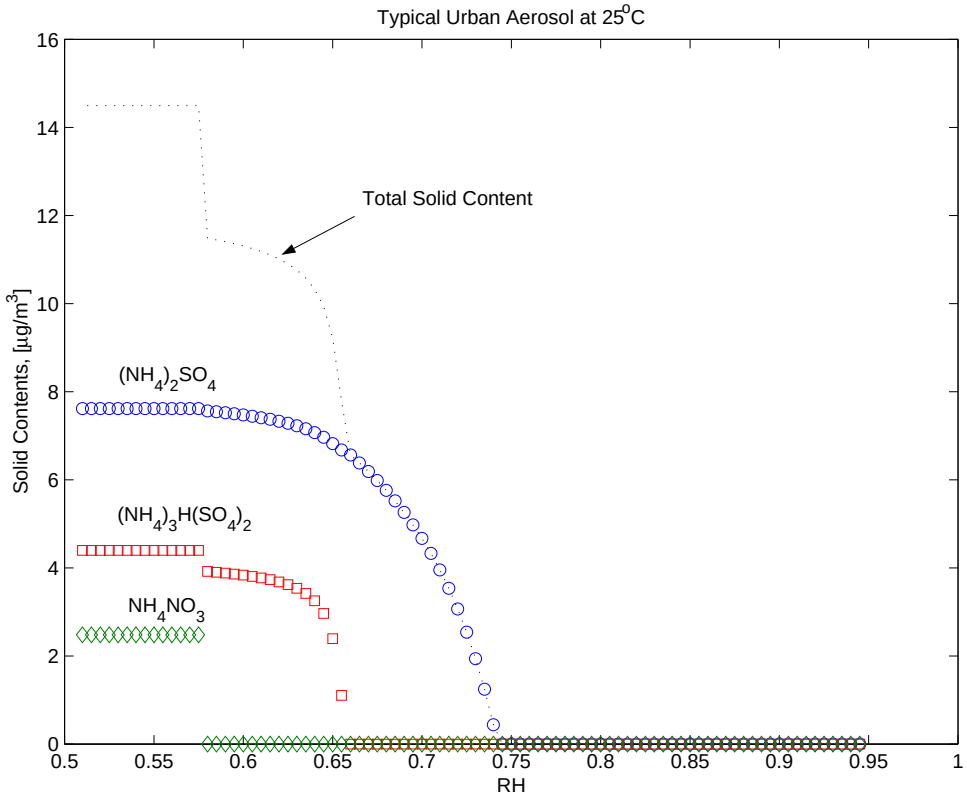
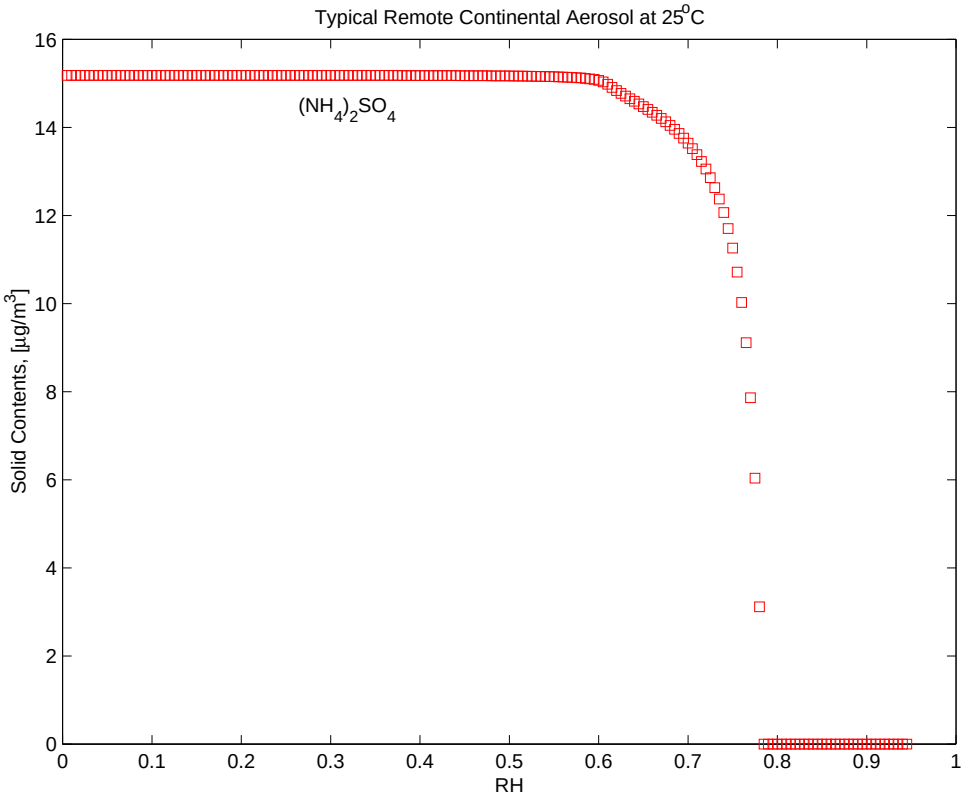


Figure 5.7: Evolution of solid content of aerosol in Figure 5.5. $W_0 = 15.665 \mu g/m^3$.



Chapter 6

Conclusions

We have developed the modeling of atmospheric inorganic aerosols 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 is investigated.

A numerical method for the solution of this optimization problem has been studied. The model 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.

Bibliography

[1] N. R. Amundson, A. Caboussat, J.-W. He, A. V. Martynenko, V. B. Savarin, J. H. Seinfeld, and K.-Y. Yoo. A New Inorganic Atmospheric Aerosol Phase Equilibrium Model (UHAERO). *Atmospheric Chemistry and Physics*, 6:975–992, 2006.

[2] NR Amundson, A Caboussat, JW He, AV Martynenko, VB Savarin, JH Seinfeld, KY Yoo, et al. A Computationally Efficient Inorganic Atmospheric Aerosol Phase Equilibrium Model (UHAERO). *Atmospheric Chemistry and Physics*, 5:9291–9324, 2005.

[3] NR Amundson, A Caboussat, JW He, and JH Seinfeld. Primal-Dual Interior-Point Method for an Optimization Problem Related to the Modeling of Atmospheric Organic Aerosols. *Journal of Optimization Theory and Applications*, 130(3):377–409, 2006.

[4] NR Amundson, A Caboussat, JW He, JH Seinfeld, and KY Yoo. Primal-Dual Active-Set Algorithm for Chemical Equilibrium Problems Related to the Modeling of Atmospheric Inorganic Aerosols. *Journal of Optimization Theory and*

Applications, 128(3):469–498, 2006.

[5] A. S. Ansari and S. N. Pandis. An Analysis of Four Models Predicting the Partitioning of Semivolatile Inorganic Aerosol Components. *Aerosol Science and Technology*, 31:129 – 153, 1999.

[6] A. S. Ansari and S. N. Pandis. Prediction of Multicomponent Inorganic Atmospheric Aerosol Behavior. *Atmospheric Environment*, 33(5):745–757, 1999.

[7] M. Bassett and J. H. Seinfeld. Atmospheric Equilibrium Model of Sulfate and Nitrate Aerosol. *Atmospheric Environment*, 17(11):2237–2252, 1983.

[8] K. S. Carslaw, S. L. Clegg, and P. Brimblecombe. A Thermodynamic Model of the System HCl-HNO_3-H_2SO_4-H_2O, including Solubilities of HBr, from 200 K to 328 K. *Journal of Chemical Physics*, 99:11557–11574, 1995.

[9] S. G. Christensen and K. Thomsen. Modeling of Vapor-Liquid-Solid Equilibria in Acidic Aqueous Solutions. *Industrial and Engineering Chemistry Research*, 42:4260–4268, 2003.

[10] S. L. Clegg, P. Brimblecombe, and A. S. Wexler. Thermodynamic Model of the System H^+-NH_4^+-Na^+-SO_4^{2-}-NO_3^--Cl^--H_2O at 298.15 K. *Journal of Physical Chemistry A*, 102(12):2155 –2171, 1998.

[11] S. L. Clegg, P. Brimblecombe, and A. S. Wexler. Thermodynamic Model of the System H^+-NH_4^+-SO_4^{2-}-NO_3^--H_2O at Tropospheric Temperatures. *Journal of Physical Chemistry A*, 102(12):2137 –2154, 1998.

[12] K. Denbigh. *The Principles of Chemical Equilibrium.* Cambridge University Press, third edition, 1971.

[13] R. Fletcher. *Practical Methods of Optimization.* John Wiley and Sons, Chichester, NY, 2nd edition, 1987.

[14] A. Forsgren and W. Murray. Newton Methods for Large-Scale Linear Inequality-Constrained Minimization. *SIAM Journal on Optimization*, 7(1):162–176, 1997.

[15] P. E. Gill, W. Murray, M. A. Saunders, and M. H. Wright. Inertia-controlling Methods for General Quadratic Programming. *SIAM Review*, 33(1):1–36, 1991.

[16] N. I. M. Gould. On Practical Conditions for the Existence and Uniqueness of Solutions to the General Equality Quadratic Programming Problem. *Mathematical Programming*, 32:90–99, 1985.

[17] A. F. Izmailov and M. V. Solodov. Karush-Kuhn-Tucker Systems: Regularity Conditions, Error Bounds and a Class of Newton-type Methods. *Mathematical Programming*, 95(3):631–650, 2003.

[18] M. Z. Jacobson. Development and Application of a New Air Pollution Modeling System II: Aerosol Module Structure and Design. *Atmospheric Environment*, 31(2):131–144, 1997.

[19] M. Z. Jacobson. Development and Application of a New Air Pollution Modeling System III: Aerosol-Phase Simulations. *Atmospheric Environment*, 31(4):587–608, 1997.

[20] M. Z. Jacobson, A. Tabazadeh, and R. P. Turco. Simulating Equilibrium within Aerosols and Nonequilibrium between Gases and Aerosols. *Journal of Geophysical Research*, 101(D4):9079–9091, 1996.

[21] Y. P. Kim and J. H. Seinfeld. Atmospheric Gas-Aerosol Equilibrium III: Thermodynamics of Crustal Elements Ca^{2+}, K^{+}, and Mg^{2+}. *Aerosol Science and Technology*, 22:93–110, 1995.

[22] Y. P. Kim, J. H. Seinfeld, and P. Saxena. Atmospheric Gas-Aerosol Equilibrium I. Thermodynamic Model. *Aerosol Science and Technology*, 19:157–181, 1993.

[23] Y. P. Kim, J. H. Seinfeld, and P. Saxena. Atmospheric Gas-Aerosol Equilibrium II: Analysis of Common Approximations and Activity Coefficient Calculation Methods. *Aerosol Science and Technology*, 19:182–198, 1993.

[24] K. Kunisch and F. Rendl. An Infeasible Active Set Method for Quadratic Problems with Simple Bounds. *SIAM Journal on Optimization*, 14(1):35–52, 2003.

[25] M. Massucci, S. L. Clegg, and P. Brimblecombe. Equilibrium Partial Pressures, Thermodynamic Properties of Aqueous and Solid Phases, and Cl_2 Production from Aqueous HCl and HNO_3 and Their Mixtures. *Journal of Physical Chemistry A*, 103(21):4209–4226, 1999.

[26] C. M. McDonald and C. A. Floudas. Global Optimization and Analysis for the Gibbs Free Energy Function using the UNIFAC, WILSON and ASOG Equations. *Industrial and Engineering Chemistry Research*, 34(5):1674–1687, 1995.

[27] Z. Y. Meng, J. H. Seinfeld, P. Saxena, and Y. P. Kim. Atmospheric Gas-Aerosol Equilibrium IV: Thermodynamics of Carbonates. *Aerosol Science and Technology*, 23:131–154, 1995.

[28] A. Nenes, S. N. Pandis, and C. Pilinis. ISORROPIA: A New Thermodynamic Equilibrium Model for Multiphase Multicomponent Inorganic Aerosols. *Aquatic Geochemistry*, 4:123–152, 1998.

[29] A. Nenes, S. N. Pandis, and C. Pilinis. Continued Development and Testing of a New Thermodynamic Aerosol Module for Urban and Regional Air Quality Models. *Atmospheric Environment*, 33(10):1553–1560, 1999.

[30] J. Nocedal and S. J. Wright. *Numerical Optimization*. Springer Series in Operations Research. Springer, New York, NY, 1999.

[31] C. Pilinis. Modeling Atmospheric Aerosols using Thermodynamical Arguments - A Review. *Global Nest: the International Journal*, 1:5–13, 1999.

[32] C. Pilinis and J. H. Seinfeld. Continued Development of a General Equilibrium Model for Inorganic Multicomponent Atmospheric Aerosols. *Atmospheric Environment*, 21:2453–2466, 1987.

[33] P. Saxena, A. B. Hudischewskyj, C. Seigneur, and J. H. Seinfeld. A Comparative Study of Equilibrium Approaches to the Chemical Characterization of Secondary Aerosols. *Atmospheric Environment*, 20:1471–1483., 1986.

[34] J. H. Seinfeld and S. N. Pandis. *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*. Wiley, New York, NY, 1998.

[35] K. Thomsen and P. Rasmussen. Modeling of Vapor-Liquid-Solid Equilibrium in Gas-Aqueous Electrolyte Systems. *Chemical Engineering Science*, 54:1787 – 1802, 1999.

[36] A. S. Wexler and J. H. Seinfeld. Second-Generation Inorganic Aerosol Model. *Atmospheric Environment*, 25A:2731–2748, 1991.

[37] K.-Y. Yoo, J.-W. He, and N. R. Amundson. Canonical Form and Mathematical Interpretation of Electrolyte Solution Systems. *Korean Journal of Chemical Engineering*, 21(2):303–307, 2004.

[38] Y. Zhang, C. Seigneur, J. H. Seinfeld, M. Jacobson, S. L. Clegg, and F. S. Binkowski. A Comparative Review of Inorganic Aerosol Thermodynamic Equilibrium Modules: Similarities, Differences, and their Likely Causes. *Atmospheric Environment*, 34:117–137, 2000.