Computational Methods for Multi-phase Multi-reaction Thermodynamic Equilibrium Problems

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INTRODUCTION

The computation of phase and chemical equilibria of water-organic-inorganic mixtures is of significant interest in atmospheric aerosol modeling. The presence of organic species in solution may substantially influence the phase transitions of the deliquescence and efflorescence of salts with changes in relative humidity. Dissolved electrolytes can have appreciable effects on the solubility of organic components in solution. At present the knowledge of aerosol composition and transformation is limited.

Our goal is to develop a computationally efficient phase equilibrium model (UHAERO) for mixed inorganic-organic atmospheric aerosols that is capable of predicting, based on minimization of the Gibbs free energy, liquid-gas, liquid-liquid, and liquid-solid equilibria, phase stability and separation.

INORGANIC AEROSOLS

The inorganic aerosol phase equilibrium module predicts inorganic gas-aerosol equilibrium. The model also computes deliquescence and crystallization behavior. The numerical minimization technique is based on a primal-dual active-set algorithm. The model is efficient and accurate for the prediction of the phase transition and multistage growth phenomena of inorganic aerosols.

CHEMICAL EQUILIBRIUM PROBLEM

The multi-reaction chemical equilibrium for a **closed inorganic aerosol system at constant temperature and pressure** and a specified element-abundance feed vector $b \in \mathbb{R}_+^{m_e}$ is the minimization problem

$$\begin{aligned} \min \quad & G(n_l, n_g, n_s) = n_l^T \mu_l + n_g^T \mu_g + n_s^T \mu_s, \\ \text{s. t.} \quad & n_l > 0, \quad n_g > 0, \quad n_s \geq 0, \\ & A_l n_l + A_g n_g + A_s n_s = b, \end{aligned}$$

where $n_\alpha \in \mathbb{R}^{m_\alpha}$, $\mu_\alpha \in \mathbb{R}^{m_\alpha}$ and $A_\alpha \in \mathbb{R}^{m_e \times m_\alpha}$ are the concentration vector, the chemical potential vector and the component-based formula matrix for the species set $\alpha = l, g, s$ respectively. The subscripts l, g, s denote the liquid, gas and solid phases respectively.

KARUSH-KUHN-TUCKER CONDITIONS

For a given set of existing solids $\bar{\mathcal{I}}_s$, the first order conditions are:

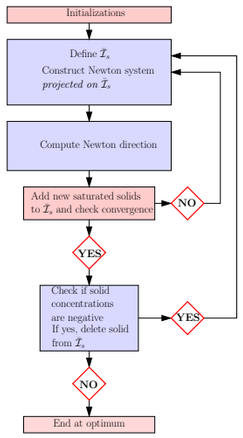
$$\begin{aligned} & \mu_l + A_l^T \lambda = 0, \\ & \mu_g + A_g^T \lambda = 0, \\ & \bar{\mu}_s + \bar{A}_s^T \lambda = 0, \quad \bar{n}_s > 0, (\text{ solids } \in \bar{\mathcal{I}}_s), \\ & \hat{\mu}_s + \hat{A}_s^T \lambda > 0, \quad \hat{n}_s = 0, (\text{ solids } \notin \bar{\mathcal{I}}_s), \\ & A_l n_l + A_g n_g + A_s n_s = b. \end{aligned}$$

The KKT first order conditions are solved with a Newton method. The phase stability or thermodynamic stability is based on the *second order conditions*.

ExUNIQUAC and PSC MODELS

The chemical potential vectors μ_α, $\alpha = g, l, s$, are given by $\mu_\alpha = \mu_\alpha^0 + RT \log a_\alpha$ where μ_α^0 is the standard chemical potential vector, R is the universal gas constant, T is the system temperature and a_α is the activity vector. For aqueous inorganic electrolyte solutions, the mole fraction-based activity coefficient is modeled by the PSC model (*Clegg et al. 1998*) or the Extended UNIQUAC model (*Thomsen, Rasmussen, 1999*).

ACTIVE-SETS/NEWTON METHOD

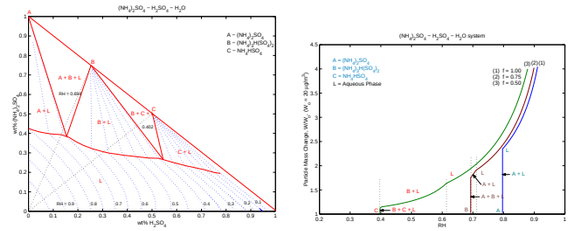


The primal-dual algorithm is based on the **active-set** strategy that provides a sequence of sets $\bar{\mathcal{I}}_s$ of solids converging to the optimal active set $\bar{\mathcal{I}}_s^\dagger$ of solid phases, *i.e.* the set of solids existing at the equilibrium.

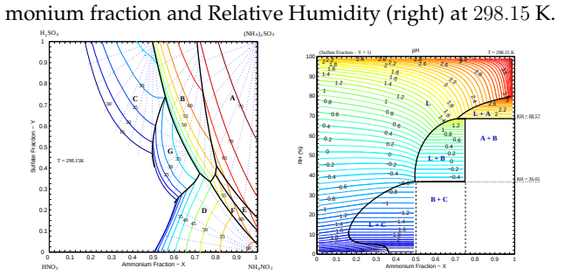
For each set $\bar{\mathcal{I}}_s$, we compute the Newton direction. If one solid salt becomes **saturated**, we introduce it into the set of **active solids** and start again a Newton method. *When the algorithm converges*, the salts with **negative concentrations** are removed from the active sets of solids salts.

SULFATE AND SULFATE/NITRATE/AMMONIUM AEROSOLS

Sulfate aerosol (ExUNIQUAC). Reconstruction of the phase diagram at 25^oC with tracking of the presence of each solid phases and evolution of the particle mass in function of RH.



Sulfate/Nitrate/Ammonium aerosol (PSC) in terms of Ammonium Fraction (X) and Sulfate Fraction (Y) (left) and Ammonium fraction and Relative Humidity (right) at 298.15 K.



The CPU time for reconstruction of these phases diagram is approximately 4.3 s. (100×100 grid points)

ORGANIC AEROSOLS

The goal is to develop a general modeling tool that is capable of predicting effectively **liquid-liquid and gas-liquid equilibria, liquid phase stability and separation of organic aerosol particles**. The Gibbs Free Energy is modeled with the **UNIFAC** model (*Fredenslund, Ghmeling, Rasmussen, 1977& 1982* for liquid-liquid or vapor-liquid equilibrium).

PHASE EQUILIBRIUM PROBLEM

The *phase equilibrium problem* for a system of n_s substances at a specified temperature T and pressure P and for a given substance-abundance vector in units of moles $b \in \mathbb{R}_+^{n_s}$ is the solution of the constrained minimization problem

$$\begin{aligned} \min \quad & G(y_\alpha, x_\alpha) = \sum_{\alpha=1}^{\pi} y_\alpha g(x_\alpha), \\ \text{s. t.} \quad & e^T x_\alpha = 1, \quad x_\alpha > 0, \quad y_\alpha \geq 0, \quad \alpha = 1, \ldots, \pi, \\ & \sum_{\alpha=1}^{\pi} y_\alpha x_\alpha = b, \end{aligned}$$

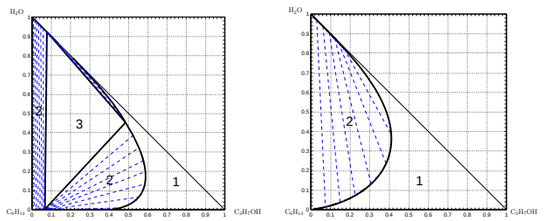
where $y_\alpha \in \mathbb{R}$ is the **total number of moles** in phase α, $x_\alpha \in \mathbb{R}_+^{n_s}$ is the composition (*e.g.*, **mole-fraction**) vector for phase α and π is the maximal number of potential phases. The phase equilibrium problem is modified by a **log/barrier penalty** for the constraints $y_\alpha \geq 0$ for the accurate detection of the existing phases:

$$\begin{aligned} \min \quad & G(y_\alpha, x_\alpha) = \sum_{\alpha=1}^{\pi} y_\alpha g(x_\alpha) - \sum_{\alpha=1}^{\pi} \nu \ln(y_\alpha), \\ \text{s. t.} \quad & e^T x_\alpha = 1, \quad x_\alpha > 0, \quad \alpha = 1, \ldots, \pi, \\ & \sum_{\alpha=1}^{\pi} y_\alpha x_\alpha = b, \end{aligned}$$

The primal-dual algorithm is based on the **interior-point** method that starts from a sequence of $\pi = n_s$ phases. At each iteration, the parameter ν is reduced and the phases that do not exist in the optimal set of equilibrium phases are deleted successively from the working set.

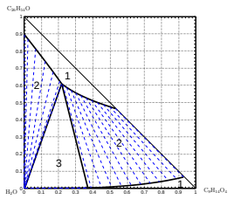
WATER-PROPANOL-HEXANE

This system involves three components (water, propanol and hexane) at $T = 211$ K. Two different UNIFAC parameterizations for liquid-liquid equilibrium give two different phase diagrams (left: *Fredenslund, 1977*, right: *Magnussen, 1981*).



The CPU time required to compute these phase diagrams is approximately 2.9 s. (100×100 grid points).

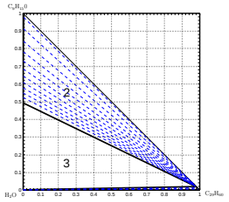
WATER-HEXACOSANOL-PINIC ACID



This system involves three components (water, hexacosanol and pinic acid). The temperature in the system is 298 K and the pressure is 1 atm. The optimum is obtained in 5 iterations of the algorithm in average.

WATER-PINONIC ACID-NONACOSANE

This system involves three components (water, pinonic acid and nonacosane). The temperature in the system is 298 K and the pressure is 1 atm. The CPU time to compute each phase diagram is approximately 5 s. (100×100 grid points).



CURRENT WORK : MIXTURES OF INORGANIC/ORGANIC AEROSOLS

We are currently developing the phase equilibrium module for mixed inorganic-organic atmospheric aerosols. A combined primal-dual interior-point and active-set method is applied for efficient numerical solution of the minimization problem:

$$\begin{aligned} \min \quad & G(y_\alpha, x_\alpha, n_l, n_s, n_g) = \sum_{\alpha=1}^{\pi} y_\alpha \, x_\alpha^T \mu_\alpha + n_g^T \mu_g + n_s^T \mu_s, \\ \text{s. t.} \quad & A_l n_l + A_s n_s + A_g n_g = b, \\ & \sum_{\alpha=1}^{\pi} y_\alpha x_\alpha = n_l, \\ & n_l > 0, \quad n_g > 0, \quad n_s \geq 0, \\ & y_\alpha \geq 0, \quad e^T x_\alpha = 1, \quad x_\alpha \geq 0, \quad \forall \alpha = 1, \ldots, \pi. \end{aligned}$$

The variable n_l is introduced to **separate the partitioning among liquid phases from the reactive part of the system consisting of the electrolytes**.

References and more informations on:

HTTP://AERO.MATH.UH.EDU

ACKNOWLEDGMENTS

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