

# Modeling and Computation of Thermodynamic Equilibrium for Mixtures of Inorganic and Organic Species

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# Motivations

Development of a thermodynamic model for mixed inorganic-organic atmospheric aerosols for the prediction of thermodynamic equilibria, phase separation, and gas/particle partitioning (UHAERO).

- *"The chemical and physical properties of aerosols are needed to estimate and predict direct and indirect climate forcing", (IPCC, 2001).*
- At present: limited knowledge of aerosol composition and transformation, high uncertainty on their environmental effects (gas-aerosol-cloud-climate interactions).
- Current aerosol models often fail to predict the phase state and composition and the multistage growth phenomena of atmospheric aerosols.



# Mixtures of Aerosol Species

- Various thermodynamic modules for inorganic aerosols (ISOROPPIA, SCAPE2, GFEMN, AIM2, ADDEM, MESA, EQSAM, etc.)
- Thermodynamic modules for pure organic-containing aerosols (*phase lock* mechanism that splits hydrophilic and hydrophobic organic components).
- The presence of organic species in solution may substantially influence phase transitions of the deliquescence and efflorescence of salts (*salt-in - salt-out effect*.) Reciprocally, dissolved electrolytes can have appreciable effects on the solubility of organic components in solution (EQSAM3,ADDEM).
- Steps of **UHAERO**.



# Outline

- Modeling of the thermodynamics of inorganic aerosols
  - Mathematical Framework.
- Thermodynamics of aerosols containing inorganic electrolytes and dicarboxylic acids
  - Modeling and activity coefficients.
  - Computational issues.
  - Construction of phase diagrams.
- Thermodynamics of aerosols containing inorganic electrolytes and organic compounds
  - Modeling of phase separation and chemical reactions.
  - Preliminary numerical results.



# Thermodynamics of Inorganic Aerosols

$$\min \quad G(\mathbf{n}_l, \mathbf{n}_s, \mathbf{n}_g) = \mathbf{n}_g^T \boldsymbol{\mu}_g + \mathbf{n}_l^T \boldsymbol{\mu}_l + \mathbf{n}_s^T \boldsymbol{\mu}_s \quad \leftarrow \text{Gibbs free energy}$$

$$\text{s. t.} \quad \mathbf{A}_g \mathbf{n}_g + \mathbf{A}_l \mathbf{n}_l + \mathbf{A}_s \mathbf{n}_s = \mathbf{b}, \quad \leftarrow \text{Stoichiometry}$$

$$\mathbf{n}_g > \mathbf{0}, \quad \mathbf{n}_l > \mathbf{0}, \quad \mathbf{n}_s \geq \mathbf{0} \quad \leftarrow \text{Positive concentrations}$$

where

- $\mathbf{n}_\alpha$ ,  $\alpha = l, g, s$  are the concentrations of species in the liquid phase, gas phase, and the solid states respectively
- $\boldsymbol{\mu}_\alpha$ ,  $\alpha = l, g, s$  are the chemical potentials.
- $\mathbf{A}_\alpha$ ,  $\alpha = l, g, s$  are the stoichiometry matrices.



# Modeling the Activity Coefficients

- The chemical potential vectors are given by

$$\mu_g = \mu_g^0 + \mathcal{R}T \ln a_g,$$

$$\mu_l = \mu_l^0 + \mathcal{R}T \ln a_l,$$

$$\mu_s = \mu_s^0,$$

where  $\mu_\alpha^0$  is a constant chemical potential and  $a_\alpha(\mathbf{x})$  is the *activity function*.

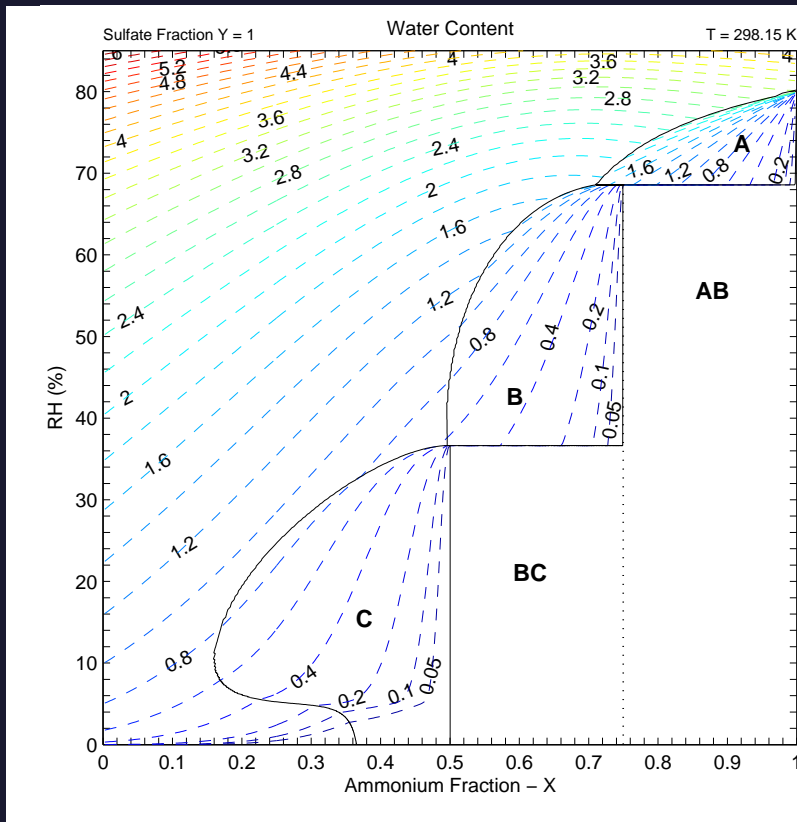
- The **PSC model** (Clegg et al., 1998) or the **ExUNIQUAC model** (Thomsen, Rasmussen, 1999) are used to describe the activity coefficients for inorganic aerosols.
- The **UNIFAC model** (Fredenslund, Gmeling, Rasmussen, 1979 & 1982) is used to describe the activity coefficients for organic aerosols.



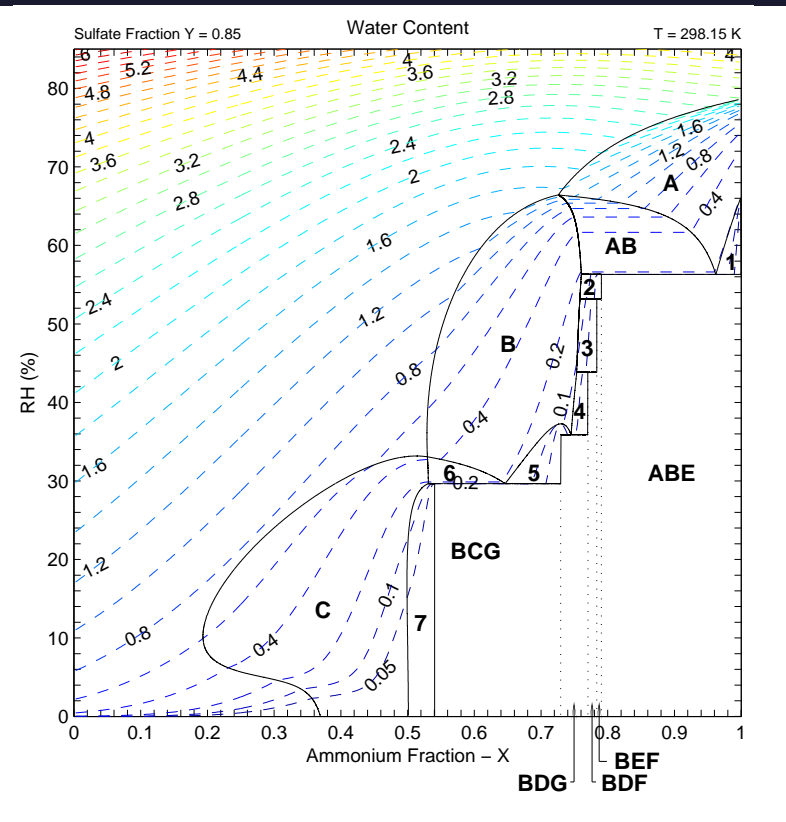
# Sulfate/Nitrate/Ammonium (PSC)

- Construction of the phase diagram for the system  $(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{SO}_4/\text{NH}_4\text{NO}_3/\text{HNO}_3/\text{H}_2\text{O}$ .

Sulfate fraction  $Y = 1$



Sulfate fraction  $Y = 0.85$



# Addition of Dicarboxylic Acids

- Addition of dicarboxylic acids increases the number of components in the liquid and gas phases.



- **Modification of the activity coefficient model** with the CSB hybrid model (*Clegg and Seinfeld, 2006*). Introduction of molal activity coefficients of an ion ( $\gamma_i$ ) and an uncharged organic solute ( $\gamma_n$ ) in the liquid mixture:

$$\ln(\gamma_i) = \Delta \ln(\gamma_i[\text{ion-water}]) + \Delta \ln(\gamma_i[\text{ion-organic}]),$$

$$\ln(\gamma_n) = \Delta \ln(\gamma_n[\text{organic-water}]) + \Delta \ln(\gamma_n[\text{ion-organic}]).$$



# Modeling of Interactions and Organic Salts

- Interactions between organic and electrolytes and water respectively, need additional assumptions (e.g. organic ions reacts only with positive inorganic ions, etc.)
- **Set of possible organic salts** to be inserted in the model is defined by the activity coefficient model.

For the succinic acid:

- $\text{H}_2\text{Succ}(s)$

And also

- $\text{NH}_4\text{HSucc}(s)$
- $(\text{NH}_4)_2\text{Succ} \cdot \text{H}_2\text{O}(s)$ .



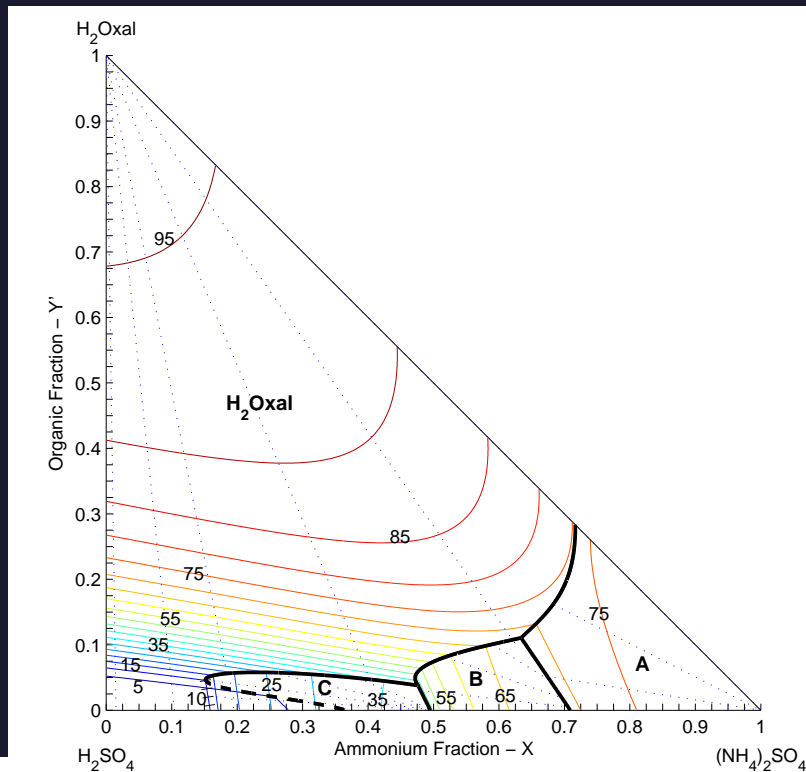
# Computational Issues

- Accuracy of the computations = Accuracy of the Energy model
  - Error due to the numerics is the rounding error.
  - No a priori information on the equilibrium state.
- Cost of the Computation = Cost of the Energy model evaluation + Cost of the numerics
  - Determination of the thermodynamic equilibrium with a **primal-dual active sets method**, with a *Newton's method* applied to the *KKT system of equations*.
  - 75% of CPU time in the evaluation of the activity coefficient model.
  - Results show that the insertion in 3D models is tractable.
- Flexibility of the Method (Black-Box Algorithm)
  - User-friendly web interface and open-source software.

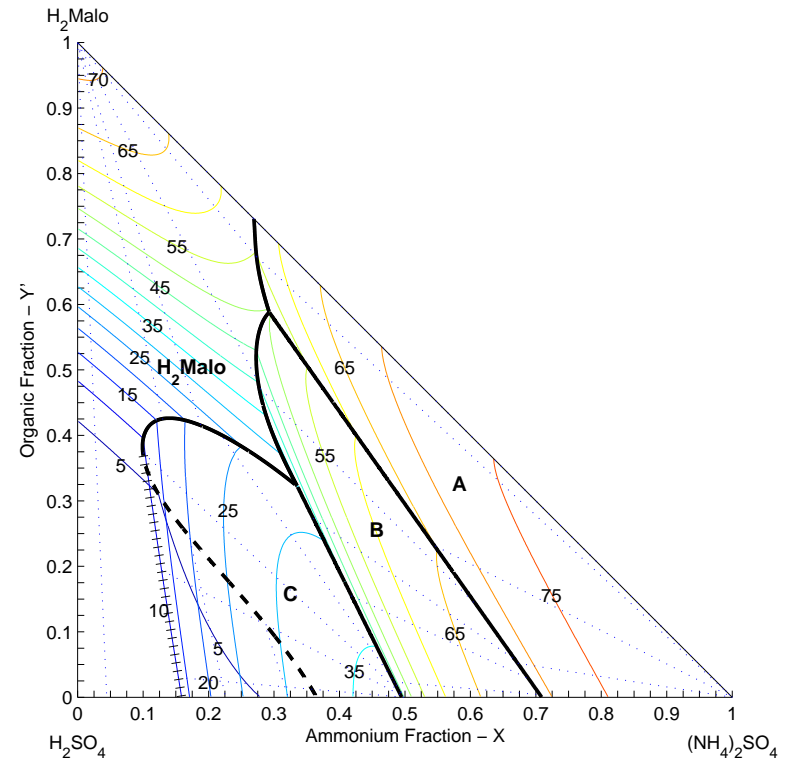
# Sulfate/Ammonium/Acid System

- Thermodynamics of particles with sulfate, ammonium and one dicarboxylic acid (oxalic, malonic, malic, glutaric, maleic, methyl succinic acids...)

Oxalic acid



Malonic acid

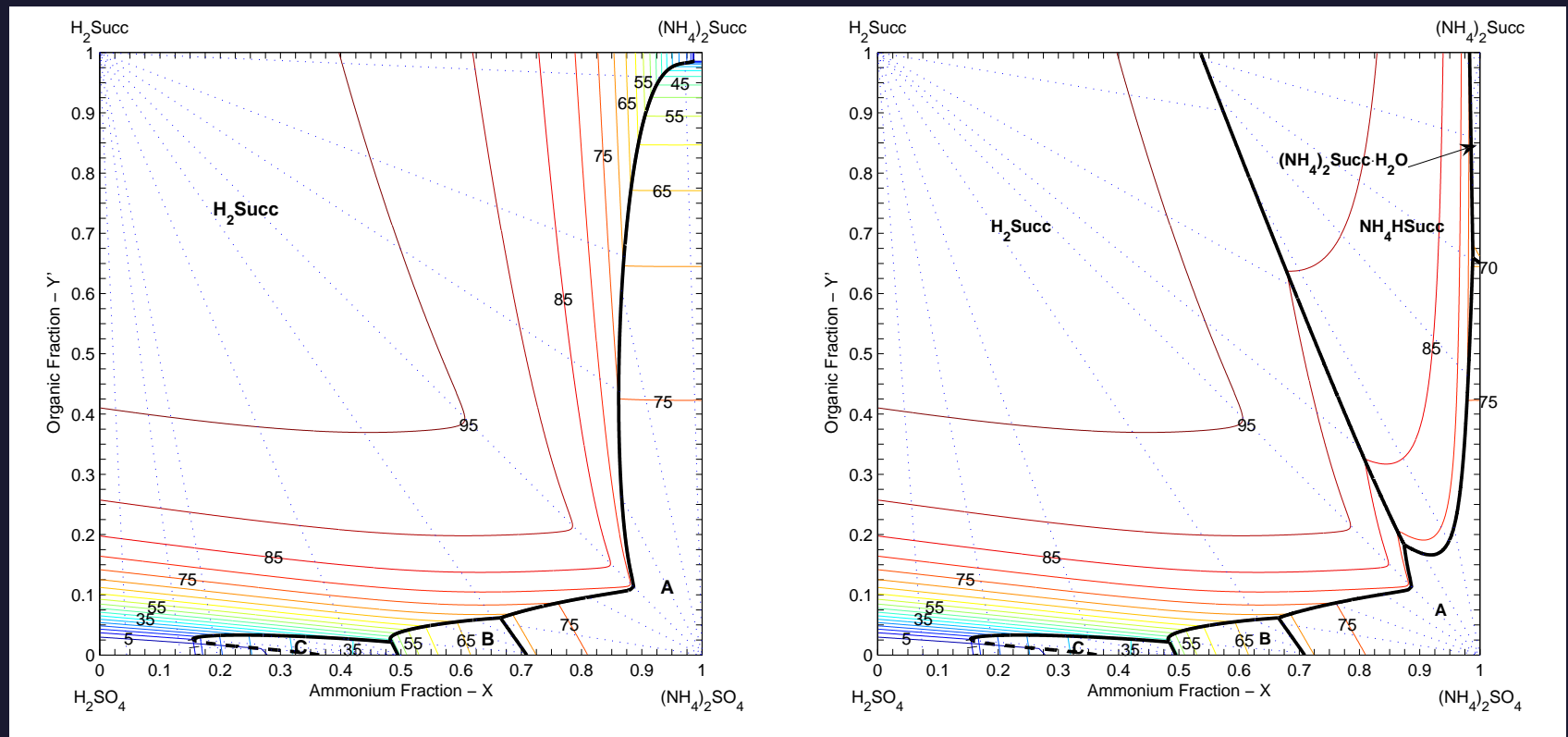


# Succinic Acid

- Sets of potential organic salts in the model :

$H_2Succ(s)$  only

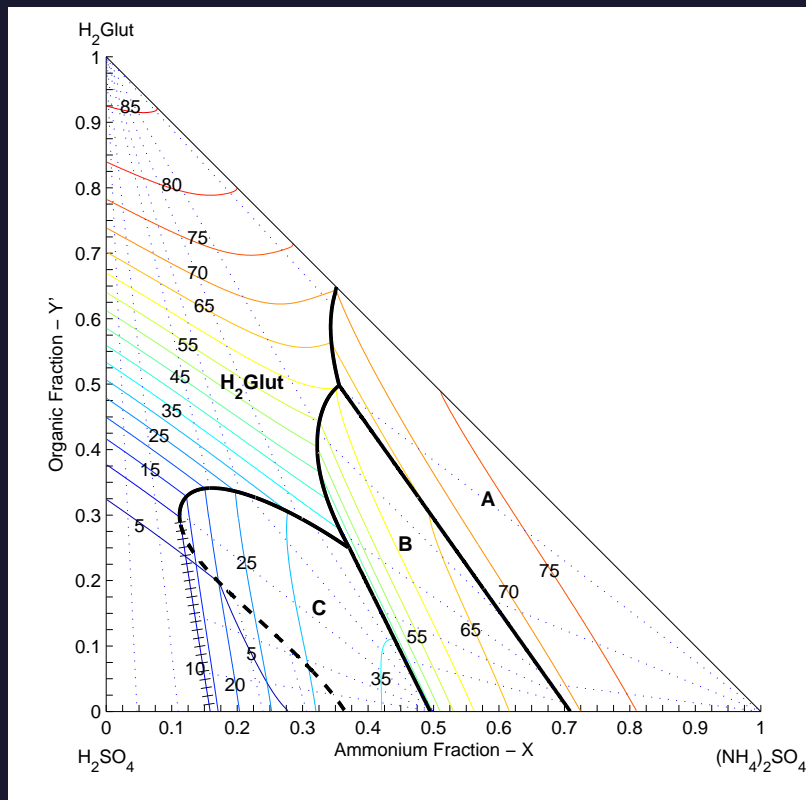
$H_2Succ(s)$ ,  $NH_4HSucc(s)$   
and  $(NH_4)_2Succ \cdot H_2O(s)$



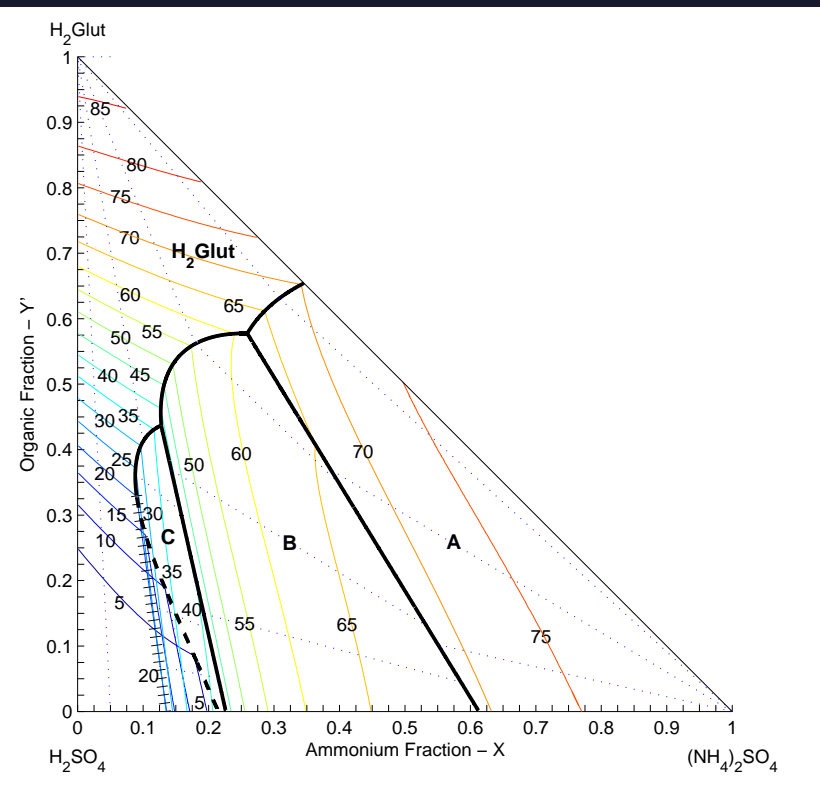
# Sensitivity Analysis

- PSC vs ExUNIQUAC for the activity coefficient model for inorganic electrolytes (sulfate/ammonium system with glutaric acid):

## PSC/UNIFAC/CSB



## ExUNIQUAC/UNIFAC/CSB



# Mixtures of Inorganic and Organic Aerosols

- Thermodynamic equilibrium for **liquid-liquid-solid-gas equilibrium** mixtures.
- Phase separation and chemical reactions, salt crystallization and dissociation of electrolytes in **each liquid phase**.
- More complex activity coefficients models (current research).
- **Splitting of the species between inorganic components, organic components and **mixed** components.**
  - Inorganic components in the aqueous phase only.
  - Reacting inorganic/organic electrolytes in the different phases.
  - Non reacting organic components in the different phases.
- At present, only the **water** is reacting in the different phases.



# Modeling the Thermodynamics

$$\min \underbrace{\sum_{\alpha=1}^P g(\mathbf{n}_\alpha)}_{\text{non-react. organics}} + \underbrace{\mathbf{n}_{l,w}^T \boldsymbol{\mu}_{l,w}}_{\text{electrolytes in all phases}} + \underbrace{\mathbf{n}_{l,i}^T \boldsymbol{\mu}_{l,i}}_{\text{electrolytes in aqueous}} + \mathbf{n}_g^T \boldsymbol{\mu}_g + \mathbf{n}_s^T \boldsymbol{\mu}_s$$

$$\text{s. t. } \sum_{\alpha=1}^P \mathbf{n}_\alpha = \begin{pmatrix} \mathbf{n}_{l,w} \\ \mathbf{b}_O \end{pmatrix} \quad \text{Mass conservation among liquid phases}$$

$$\mathbf{A}_g \mathbf{n}_g + \mathbf{A}_{l,i} \mathbf{n}_{l,i} + \mathbf{A}_{l,w} \mathbf{n}_{l,w} + \mathbf{A}_s \mathbf{n}_s = \mathbf{b}_I, \quad \text{Stoichiometry relation}$$

$$\mathbf{n}_\alpha \geq \mathbf{0}, \quad \alpha = 1, \dots, P, \quad \text{Positive organic concentrations}$$

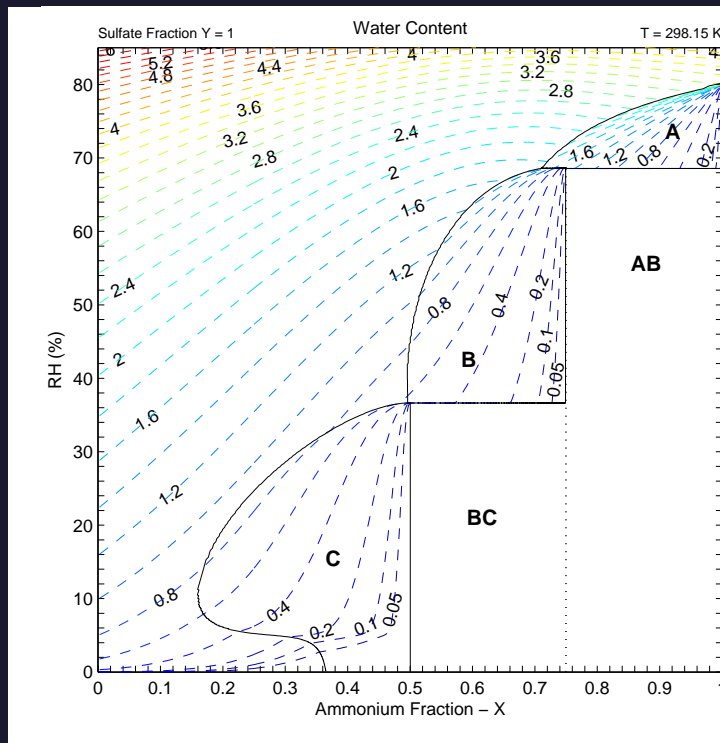
$$\mathbf{n}_{l,i}, \mathbf{n}_{l,w}, \mathbf{n}_g > \mathbf{0}, \quad \mathbf{n}_s \geq \mathbf{0} \quad \text{Positive inorganic concentrations}$$



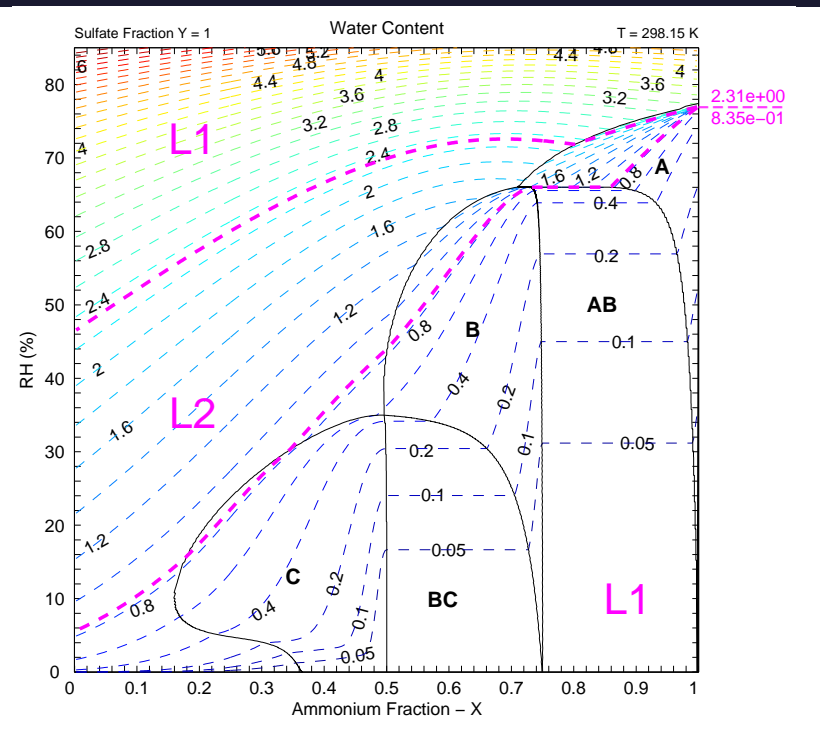
# Sulfate/Nitrate/Ammonium with Organics

- Construction of the phase diagram for the system  $(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{SO}_4/\text{NH}_4\text{NO}_3/\text{HNO}_3/\text{H}_2\text{O}$  when the system also include two organic species.

without  
organics



adipic acid and  
glutaraldehyde

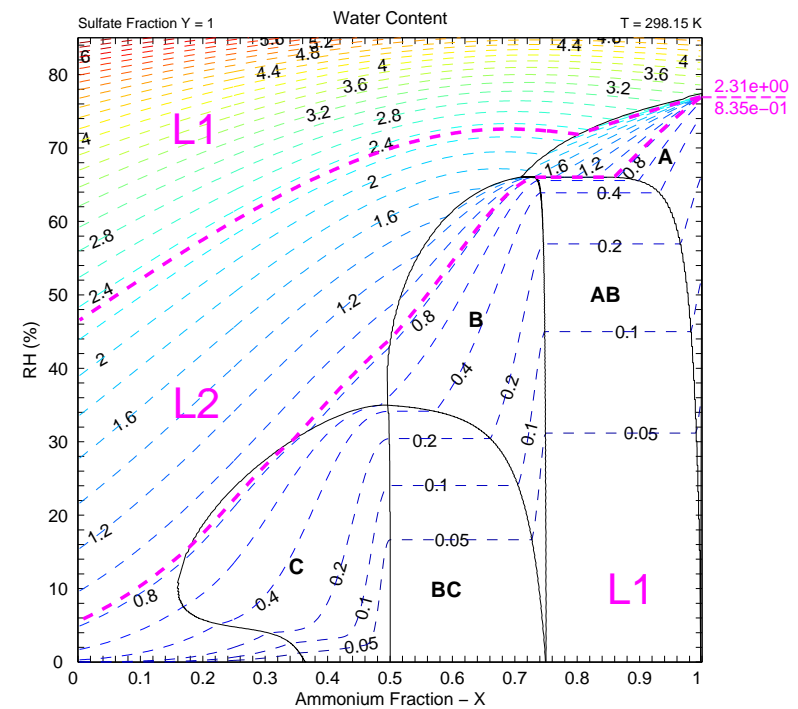
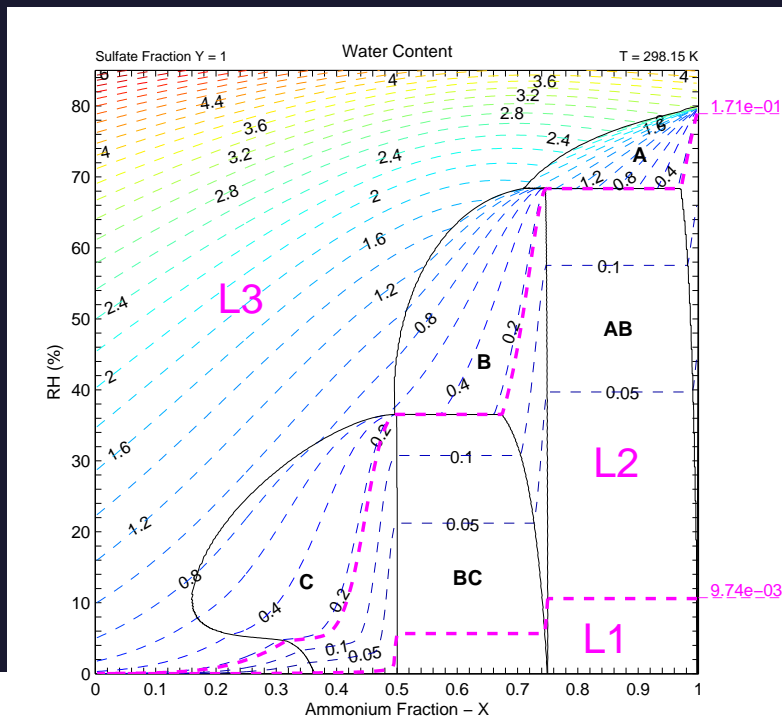


# Sulfate/Nitrate/Ammonium with Organics

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1-hexacosanol and  
pinic acid

adipic acid and  
glutaraldehyde



# Conclusions

- **Thermodynamics of mixtures of inorganic and organic aerosols.**
  - Significant impact of organics in inorganic/organic mixtures on crystallization.
  - Modeling of activity coefficients with various models (PSC, UNIFAC, CSB, etc.)
  - Framework is accurate, efficient and flexible.
- **Current Work:** Design of (more) efficient numerical methods for the determination of liquid-liquid-gas-solid thermodynamic equilibrium

*(Amundson et al, Atmos. Chem. Phys., 6, 2006)*

*(Amundson et al, J. Geophys. Res., to appear, 2007)*

*(Amundson et al, Atmos. Chem. Phys. Discuss., submitted, 2007)*



<http://aero.math.uh.edu>



The banner features the UH AERO logo on the left, which includes a stylized red 'UH' and the word 'AERO' in blue. Below the logo is the text 'Mathematical Modeling, Analysis & Computation'. To the right of the logo, there are two mathematical equations. The first is a partial differential equation: 
$$\frac{\partial n}{\partial t} + \frac{\partial}{\partial x} (In) = \frac{1}{2} \int_0^x \beta(x', x - x') n(x') n(x - x') dx' - n \int_0^{\infty} \beta(x, x') n(x') dx'$$
 The second is an optimization problem: 
$$\inf \left\{ \sum_{\alpha} y_{\alpha} f(x_{\alpha}), \sum_{\alpha} y_{\alpha} x_{\alpha} = x, \sum_{\alpha} y_{\alpha} = 1 \right\}$$