Thermodynamic Modeling of Atmospheric Inorganic Aerosols.

F.-Y. Cheng[†], J. W. He[†], **A. V. Martynenko**[†] and J. H. Seinfeld[⋆]

[†] University of Houston, Houston, TX

[⋆]California Institute of Technology, Pasadena, CA

http://aero.math.uh.edu

Thermodynamic Models

- The inorganic constituents of atmospheric particles typically consist of electrolytes of ammonium, sodium, calcium, sulfate, nitrate, chloride, carbonate, etc. The phase state of such a mixture at a given temperature and relative humidity will tend to thermodynamic equilibrium with the gas phase.
- A series of thermodynamic models such as *SEQUILIB*, *SCAPE2*, *EQUISOLVII*, and *ISORROPIA* have been developed that attempt to predict the proper ties of inorganic aerosols.
- One of the most challenging parts for the available models is the prediction of the partitioning of the inorganic aerosol components between aqueous and solid phases.
- CMAQ uses ISORROPIA model to predict gas-liquid-solid equilibrium in inorganic aerosol.
- UHAERO–Inorganic Module: a new thermodynamic equilibrium model for multicomponent inorganic aerosols.

Differences of the Models

1. **Difference in activity coefficient models:**
   - ISORROPIA uses Bromley's model (1973) and the Kusik and Meissner model (1978) for calculation of activity coefficients.
   - UHAERO incorporates **PSC** (*Clegg et al., 1998*) and the **Extended UNIQUAC** (**ExUNIQUAC**) (*Thomsen, Rasmussen, 1999*) mole fraction based activity coefficients models.
2. **Difference in prediction of the aerosol water content:**
   - ISORROPIA relies on the standard ZSR equation to estimate the aerosol water content.
   - UHAERO. The aerosol water content is directly calculated during the computational process from the activity coefficient model.
3. **Difference in prediction of solid phase:**
   - ISORROPIA relies on *a priori* knowledge of the presence of phases at a certain relative humidity and overall composition.
   - UHAERO detects crystallization in computational process.
4. **Difference in solution method:**
   - ISORROPIA uses reaction oriented approach to describe the chemical equilibrium.
   - UHAERO is based on *canonical formulation* of the electrolyte solution system.

Modeling Thermodynamic Equilibrium. UHAERO

- Optimality conditions:

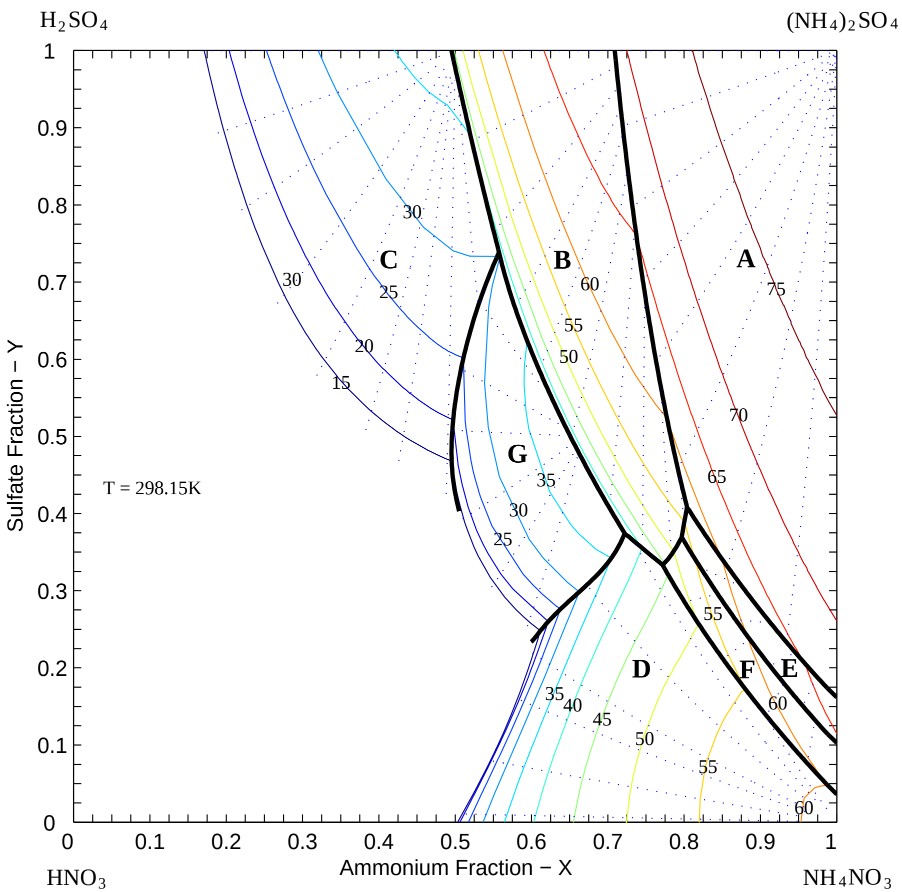
$$
\begin{aligned}
&\boldsymbol{\mu}_g + \mathbf{A}_g^T \lambda = 0, \\
&\boldsymbol{\mu}_l + \mathbf{A}_l^T \lambda = 0, \\
&\mathbf{n}_s \geq 0, \quad \boldsymbol{\mu}_s + \mathbf{A}_s^T \lambda \geq 0, \quad \mathbf{n}_s^T (\boldsymbol{\mu}_s + \mathbf{A}_s^T \lambda) = 0, \\
&\mathbf{A}_g \mathbf{n}_g + \mathbf{A}_l \mathbf{n}_l + \mathbf{A}_s \mathbf{n}_s = \mathbf{b}.
\end{aligned}
$$

  - $\mathbf{n}_g$, $\mathbf{n}_l$, $\mathbf{n}_s$: concentration vectors in gas, liquid, and solid phases,
  - $\mathbf{A}_g$, $\mathbf{A}_l$, $\mathbf{A}_s$: component-based formula matrices,
  - $\mathbf{b}$ is the component-based feed vector,
  - chemical potential vectors:

$$
\begin{aligned}
\boldsymbol{\mu}_g &= \boldsymbol{\mu}_g^0 + RT \ln \boldsymbol{a}_g, \\
\boldsymbol{\mu}_l &= \boldsymbol{\mu}_l^0 + RT \ln \boldsymbol{a}_l, \\
\boldsymbol{\mu}_s &= \boldsymbol{\mu}_s^0,
\end{aligned}
$$

- *A primal-dual active set/Newton algorithm* is used for the efficient and accurate solution of thermodynamic equilibrium problems related to modeling of atmospheric inorganic aerosols.

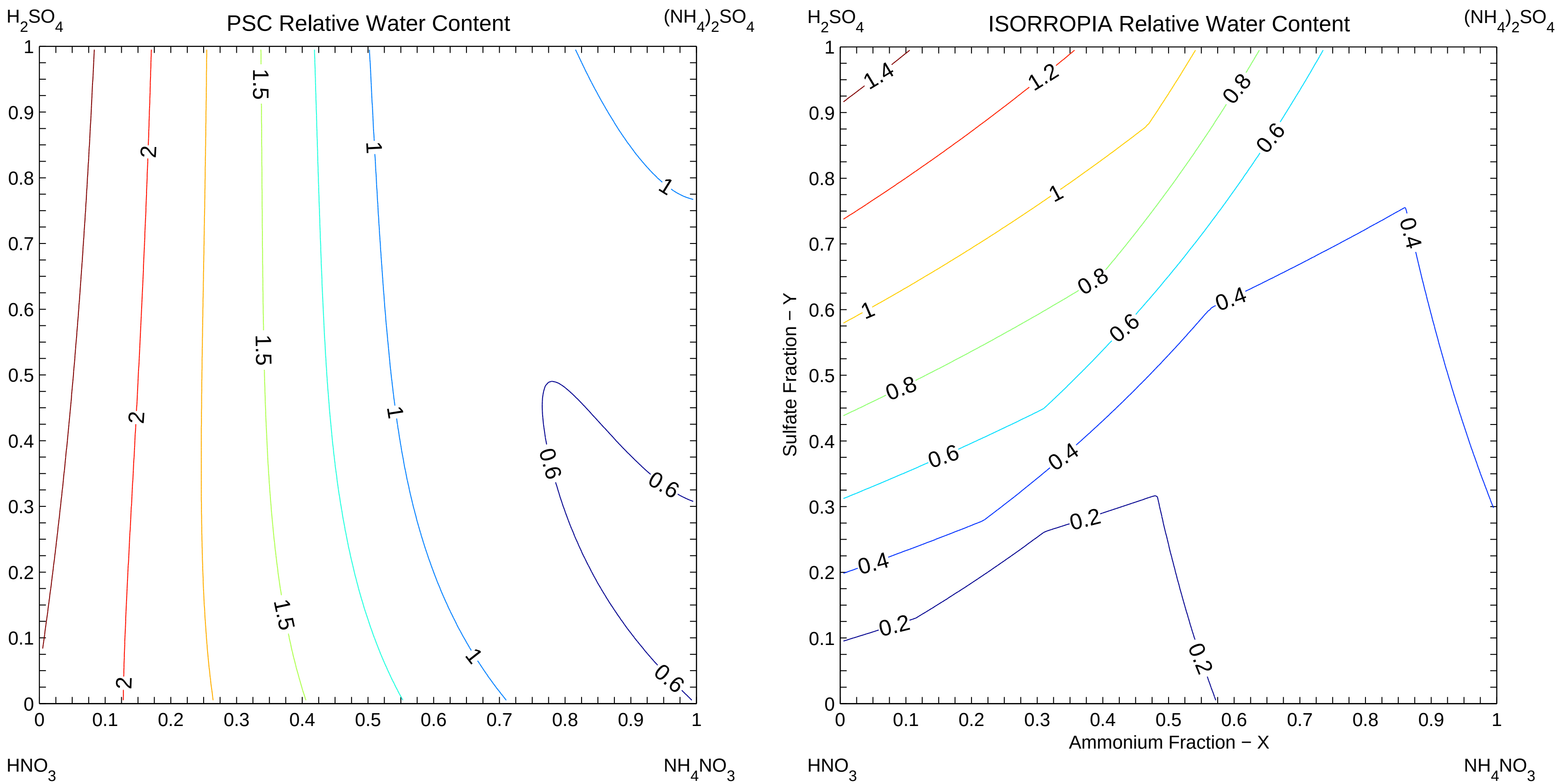
Ammonium/Sulfate/Nitrate Phase Diagram at 298.15 K



- Ammonium fraction
$$X = \frac{[NH_4^+]}{[NH_4^+] + [H^+]}$$
- Sulfate fraction
$$Y = \frac{[SO_4^{2-}]}{[SO_4^{2-}] + [NO_3^-]}$$
- Seven possible solid phases exist in this system, labeled as
  A = $(NH_4)_2SO_4$
  B = $(NH_4)_3H(SO_4)_2$
  C = NH_4HSO_4
  D = NH_4NO_3
  E = $2NH_4NO_3 \cdot (NH_4)_2SO_4$
  F = $3NH_4NO_3 \cdot (NH_4)_2SO_4$
  G = $NH_4NO_3 \cdot NH_4HSO_4$

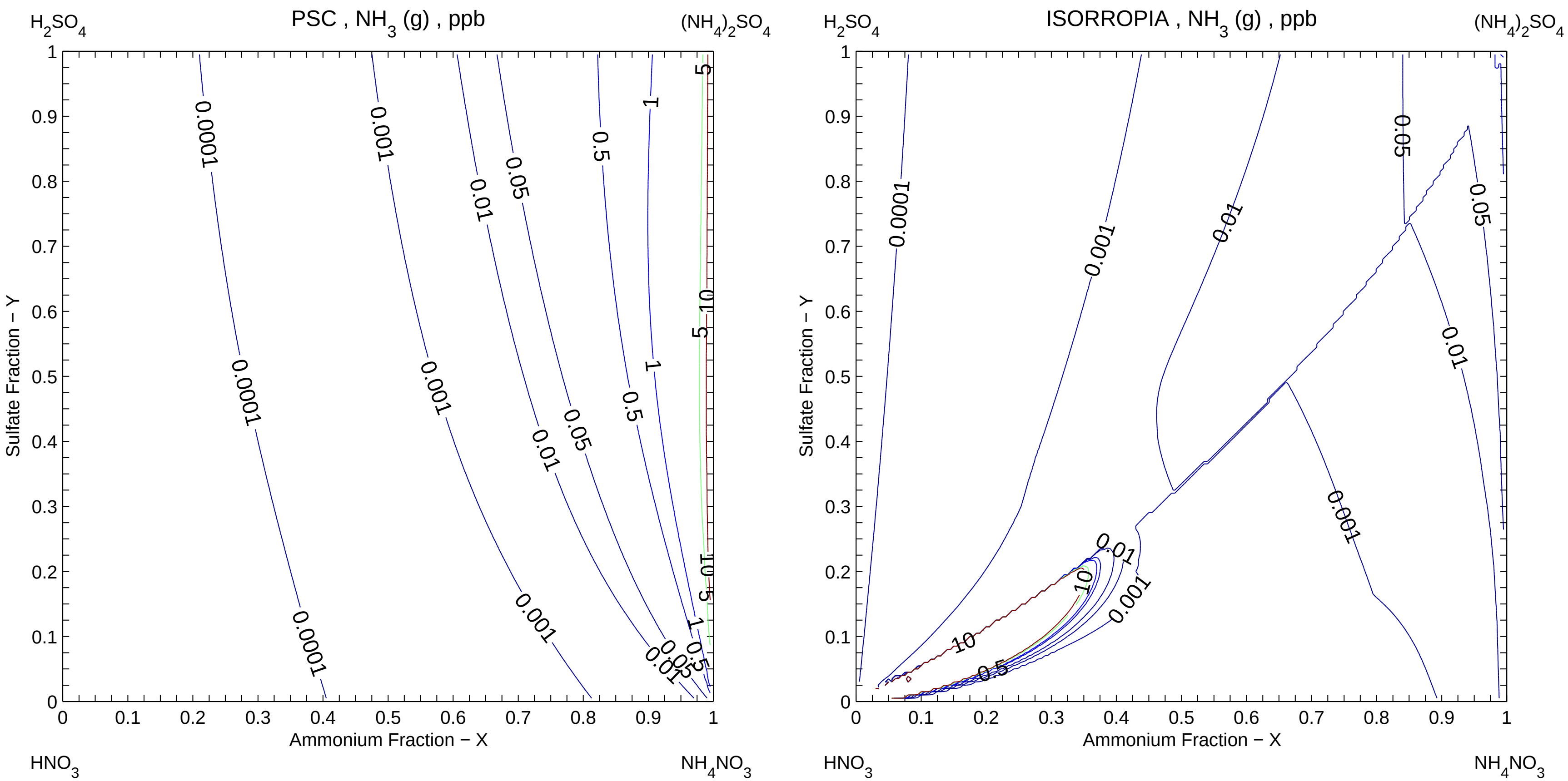
- Regions outlined by heavy black lines show the first solid that reaches saturation with decreasing RH.
- The thin labeled solid lines are water activity contours at saturation.
- The dotted lines are the so-called liquidus lines introduced by Potukuchi and Wexler (1995).

Phase diagram at $T = 283.15K$, $RH = 50\%$



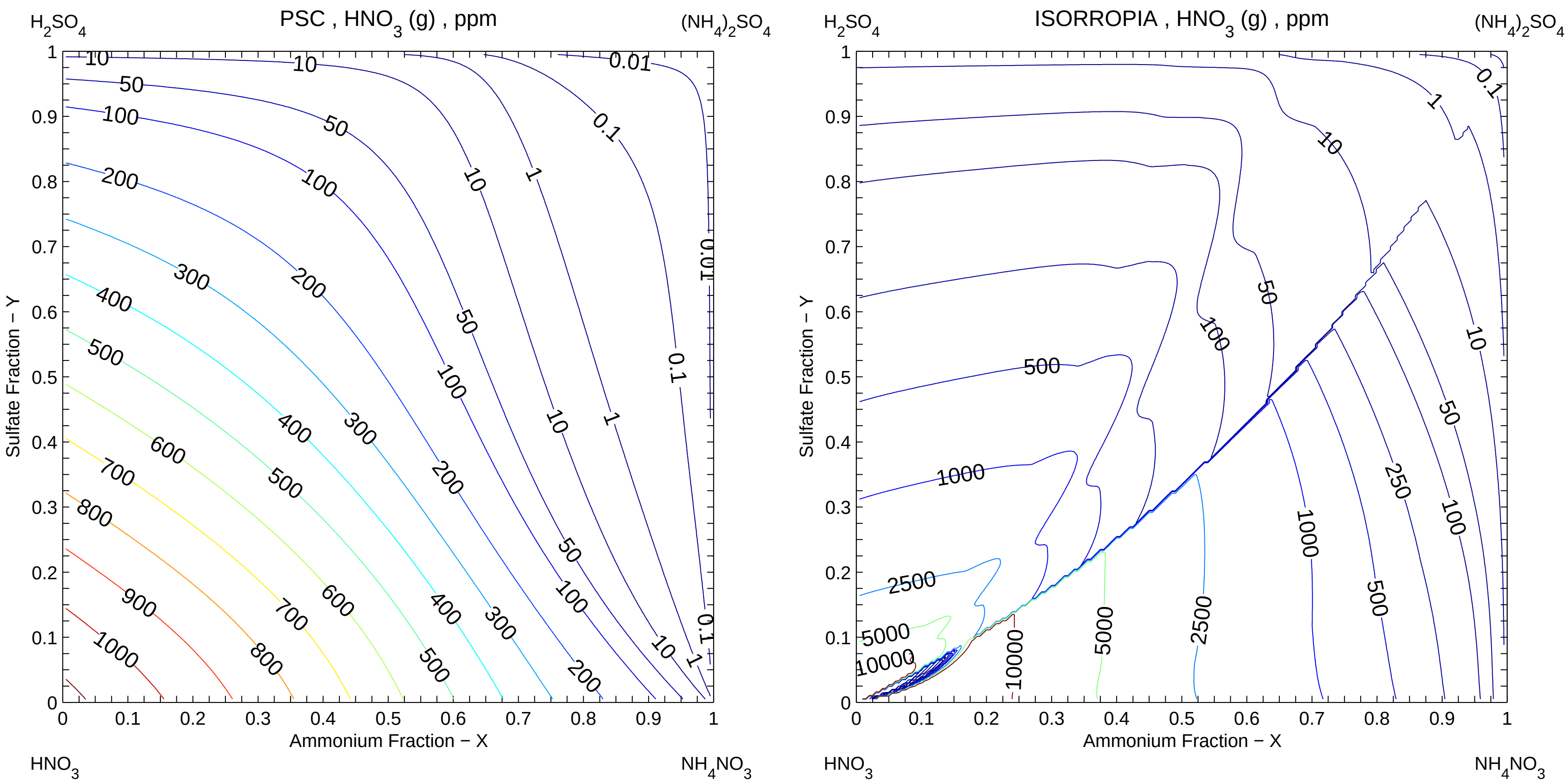
- Isolines of relative water content for two models.
- Metastable equilibrium (no solid phase), open system (reverse ISORROPIA mode).

Phase diagram at $T = 283.15K$, $RH = 50\%$



- Isolines of concentration of NH_3 in gas phase for two models.
- Metastable equilibrium (no solid phase), open system (reverse ISORROPIA mode).

Phase diagram at $T = 283.15K$, $RH = 50\%$



- Isolines of concentration of HNO_3 in gas phase for two models.
- Metastable equilibrium (no solid phase), open system (reverse ISORROPIA mode).

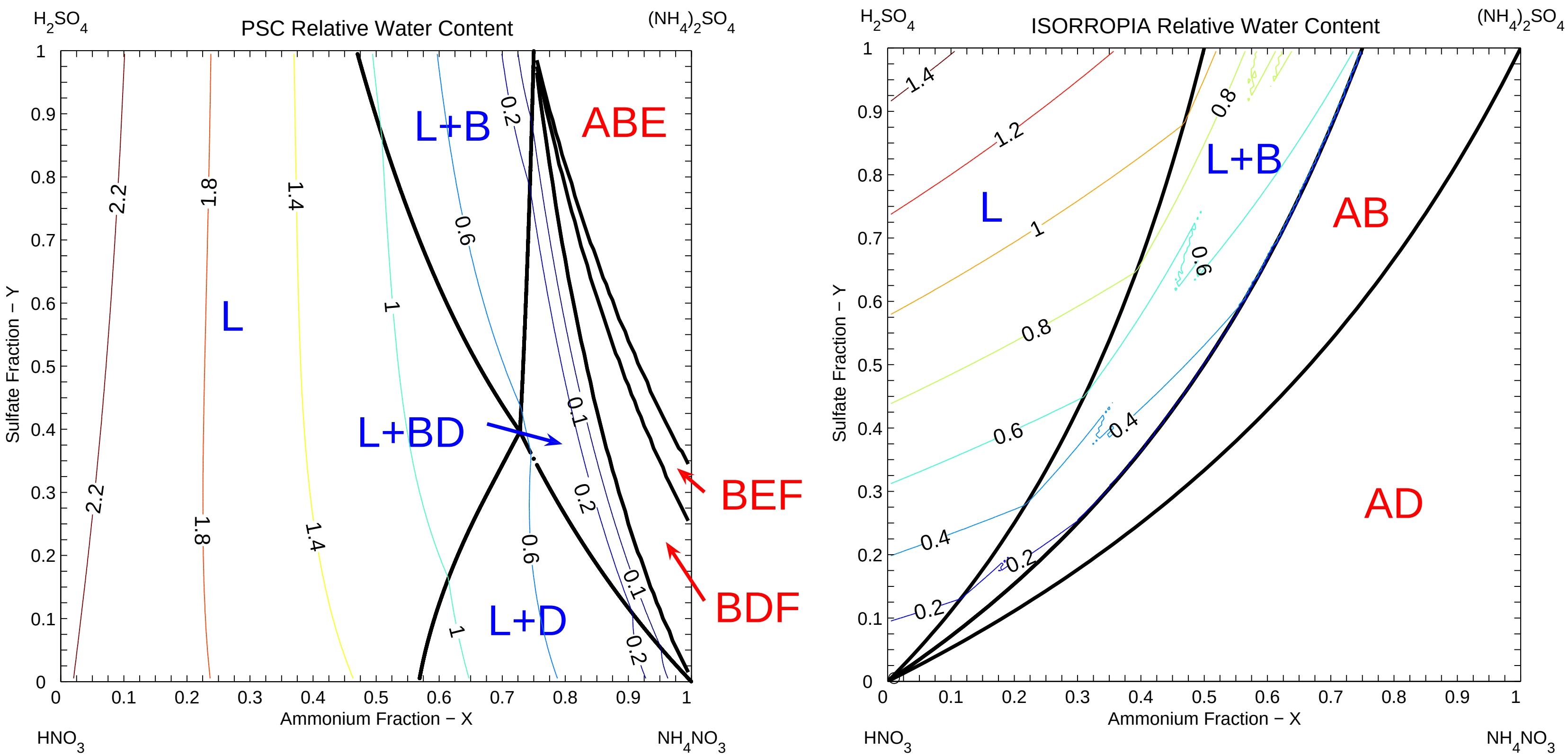
Andrey Martynenko, University of Houston, andrey@math.uh.edu

Phase diagrams in presence of solid phase

Seven possible salts may exist in the system:

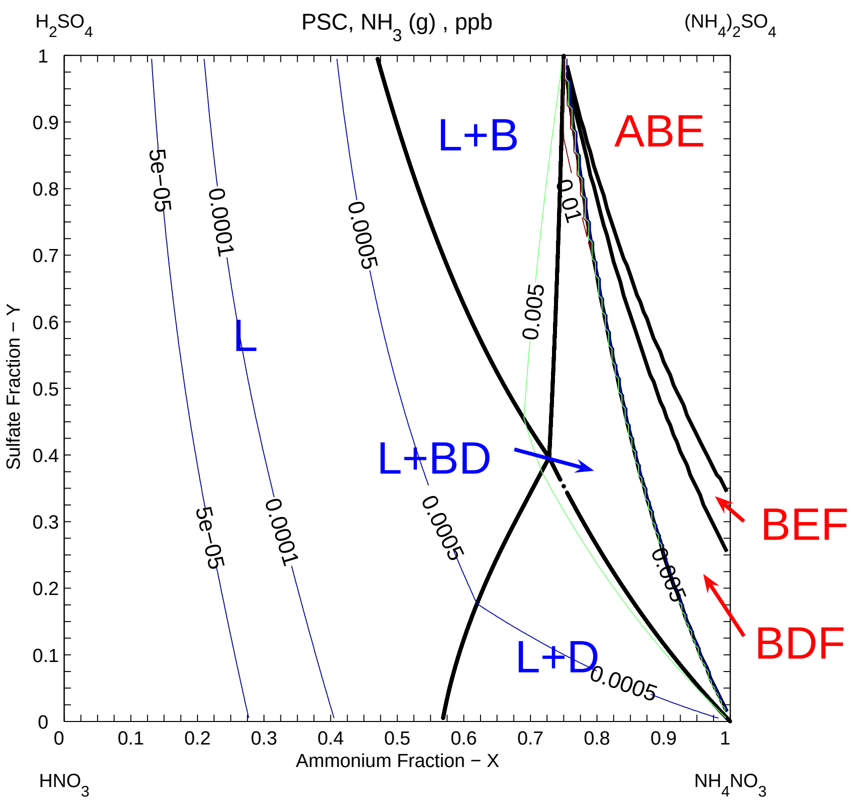
$A = (NH_4)_2SO_4$	(AS),
$B = (NH_4)_3H(SO_4)_2$	(LET),
$C = NH_4HSO_4$	(AHS),
$D = NH_4NO_3$	(AN),
$E = 2NH_4NO_3 \cdot (NH_4)_2SO_4$	(2AN·AS),
$F = 3NH_4NO_3 \cdot (NH_4)_2SO_4$	(3AN·AS),
$G = NH_4NO_3 \cdot NH_4HSO_4$	(AN·AHS).

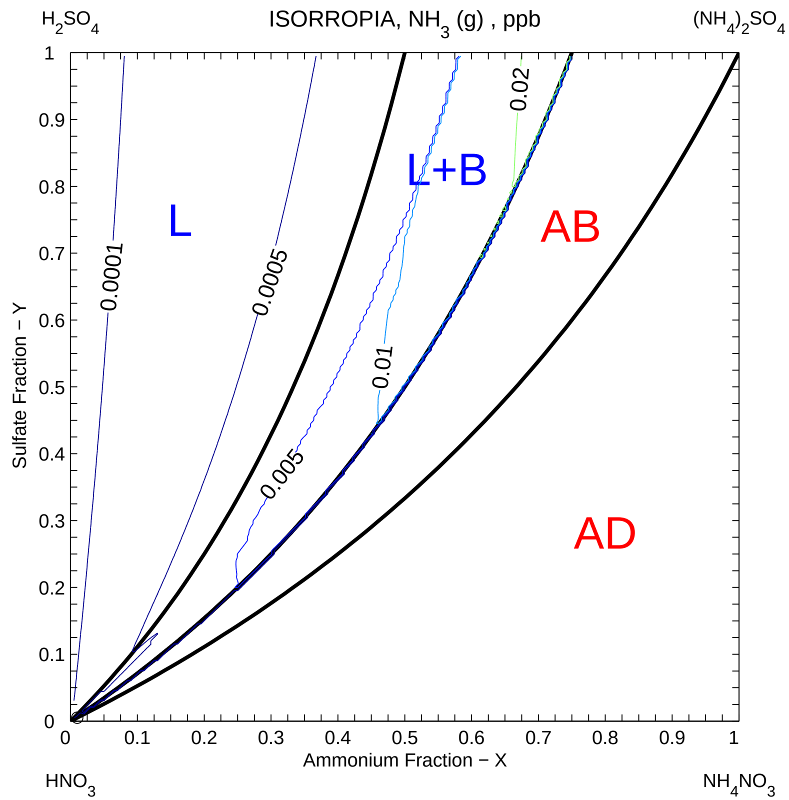
Phase diagram at $T = 283.15K$, $RH = 50\%$



- Isolines of water content for two models.
- Heavy black lines outline the regions where indicated salts exist in solid phase.
- Red colored salts indicate a dry particle, blue colored – liquid particle.
- Open system (reverse ISORROPIA mode).

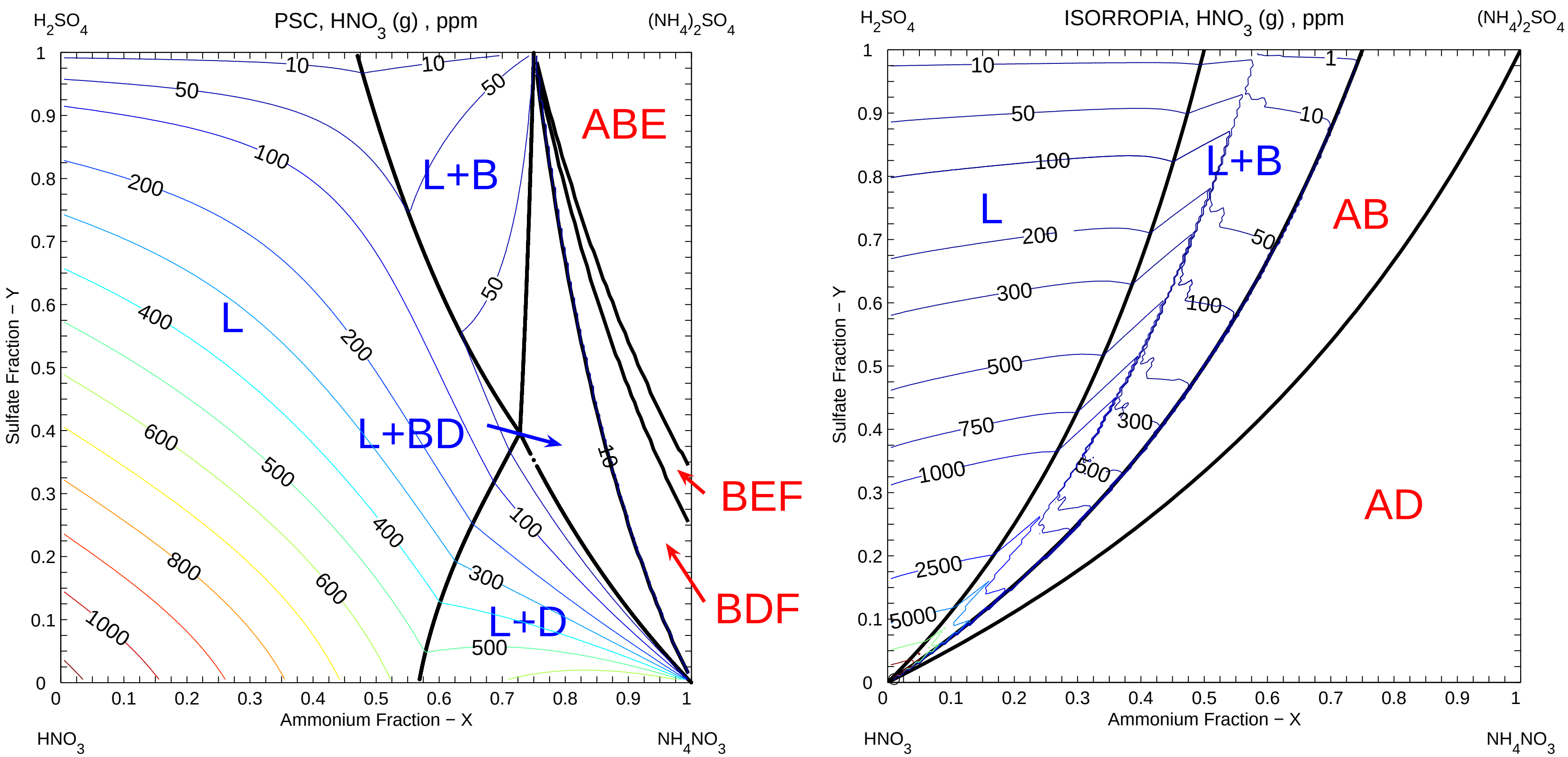
Phase diagram at $T = 283.15K$, $RH = 50\%$





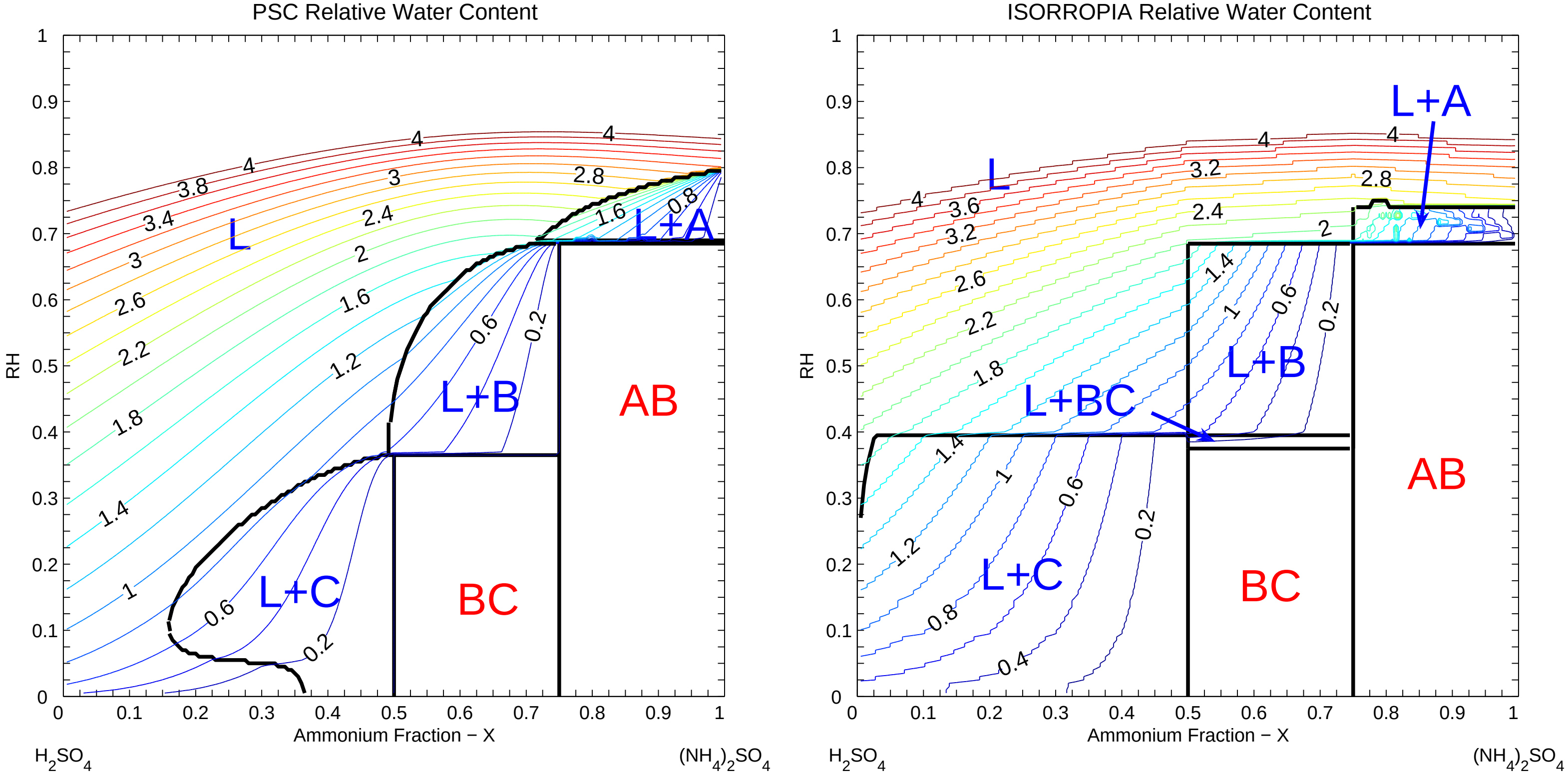
- Isolines of concentration of NH_3 in gas phase for two models.
- Heavy black lines outline the regions where indicated salts exist in solid phase.
- Red colored salts indicate a dry particle, blue colored – liquid particle.
- Open system (reverse ISORROPIA mode).

Phase diagram at $T = 283.15K$, $RH = 50\%$



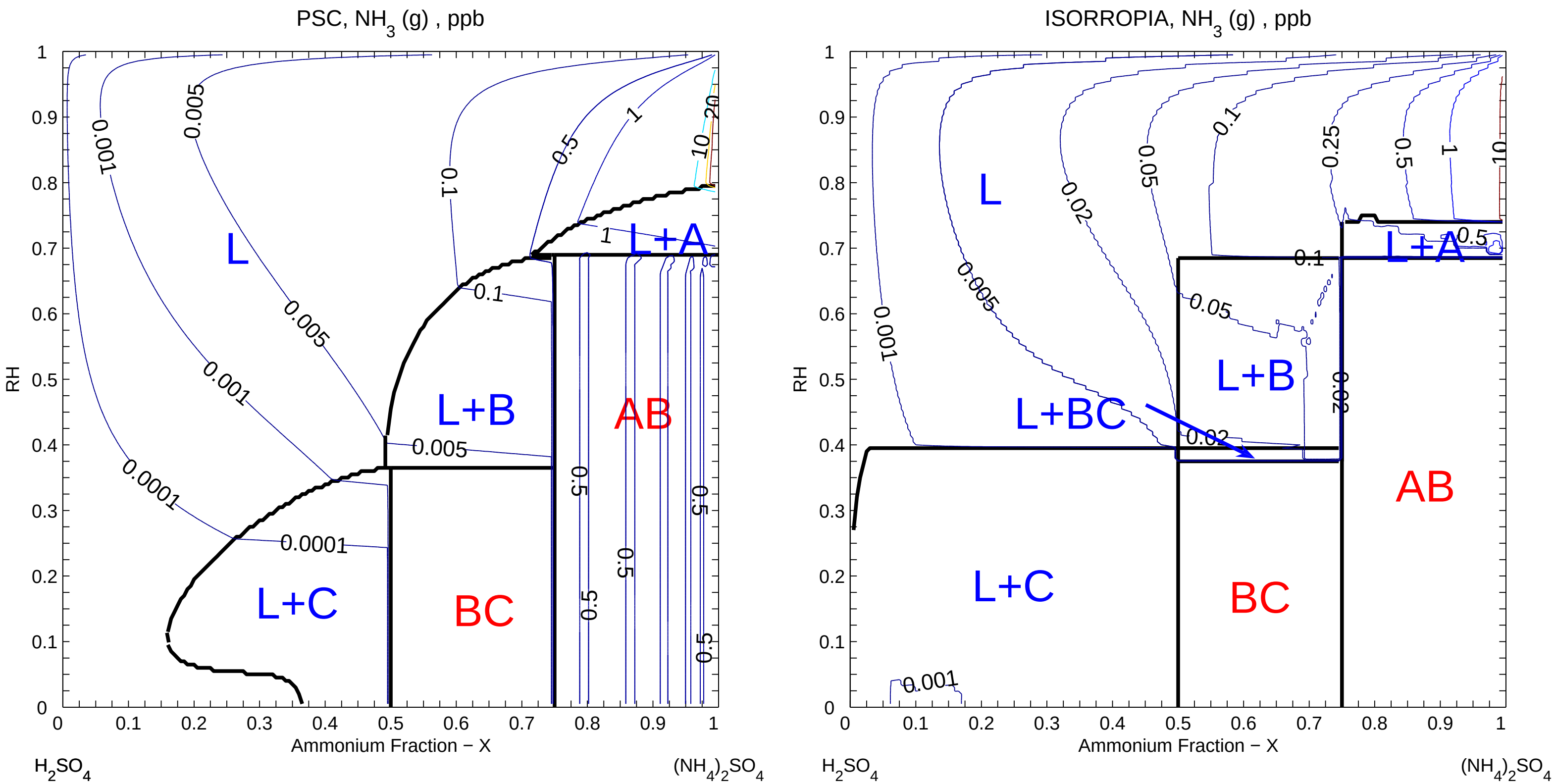
- Isolines of concentration of HNO_3 in gas phase for two models.
- Heavy black lines outline the regions where indicated salts exist in solid phase.
- Red colored salts indicate a dry particle, blue colored – liquid particle.
- Open system (reverse ISORROPIA mode).

Ammonium/Sulfate Phase Diagram at $T = 298.15K$



- Isolines of water content for two models.
- Heavy black lines outline the regions where indicated salts exist in solid phase.
- Red colored salts indicate a dry particle, blue colored – liquid particle.
- Open system (reverse ISORROPIA mode).

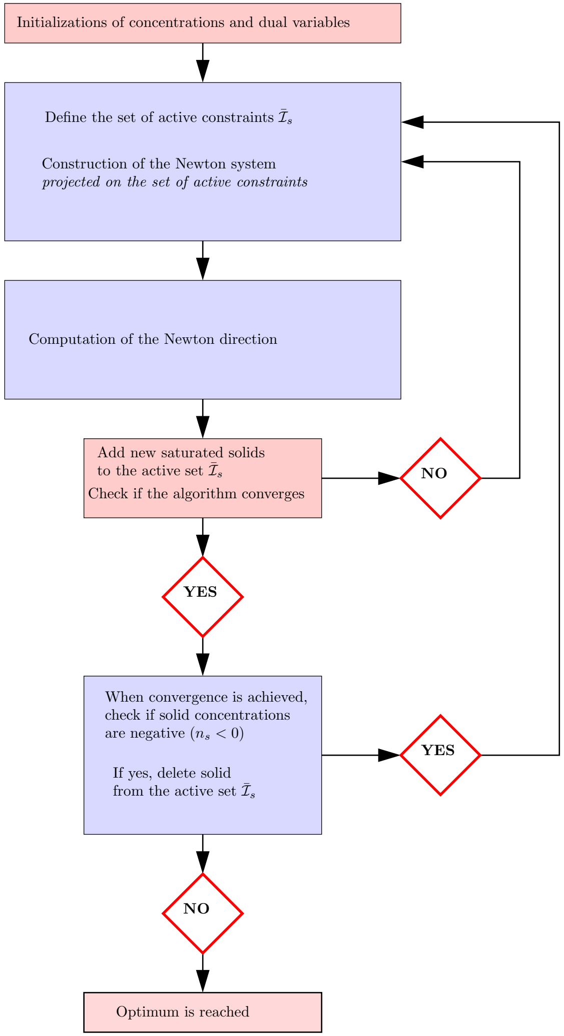
Ammonium/Sulfate Phase Diagram at $T = 298.15K$



- Isolines of concentration of NH_3 in gas phase for two models.
- Heavy black lines outline the regions where indicated salts exist in solid phase.
- Red colored salts indicate a dry particle, blue colored – liquid particle.
- Open system (reverse ISORROPIA mode).

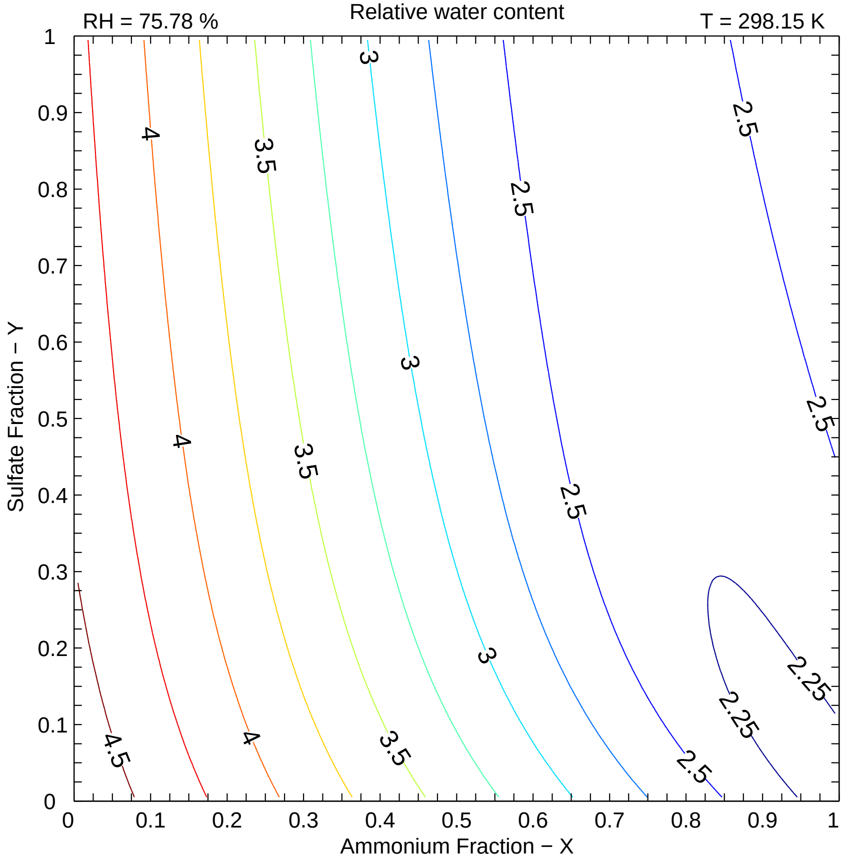
http://aero.math.uh.edu

UHAERO-Inorganic Module

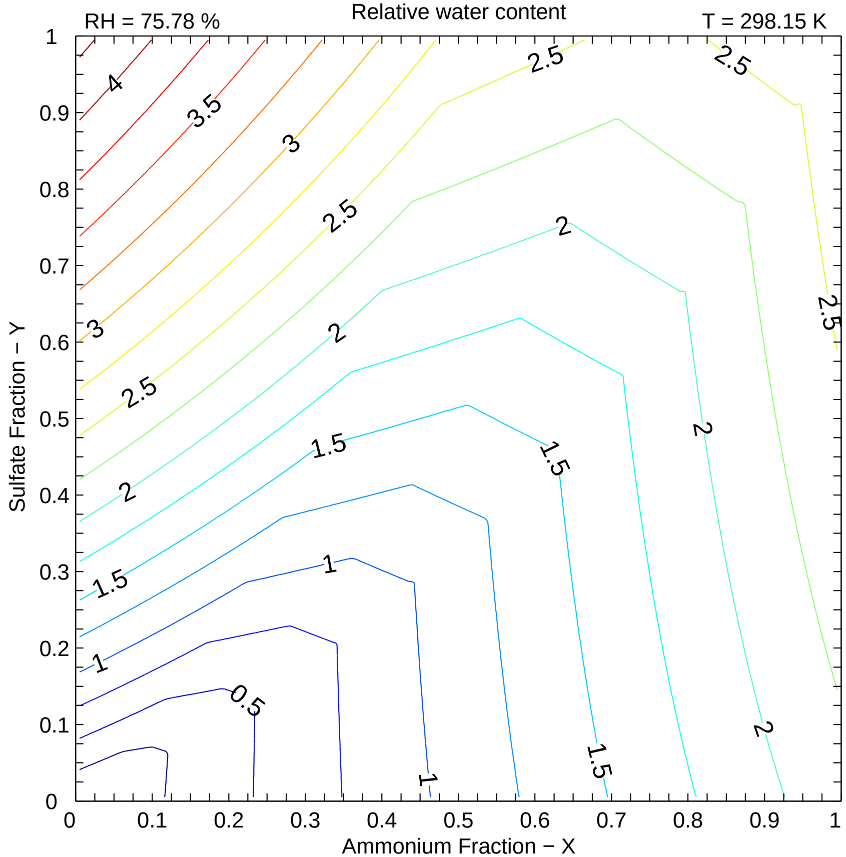


- UHAERO-Inorganic Module can be run in two modes: (1) the water content in the system is specified; (2) the system is equilibrated to a fixed relative humidity (RH).
- In case (2), the aerosol water content is directly computed from the minimization process, i.e., without using an empirical relationship such as the ZSR equation.
- The water activity is predicted using either PSC or ExUNIQUAC.
- The equilibration of trace gases between the vapor and condensed phases can be enabled or disabled as required, as can the formation of solids, which allows the properties of liquid aerosols supersaturated with respect to solid phases to be investigated.

Phase diagram at $T = 298.15K$, $RH = 75.78\%$



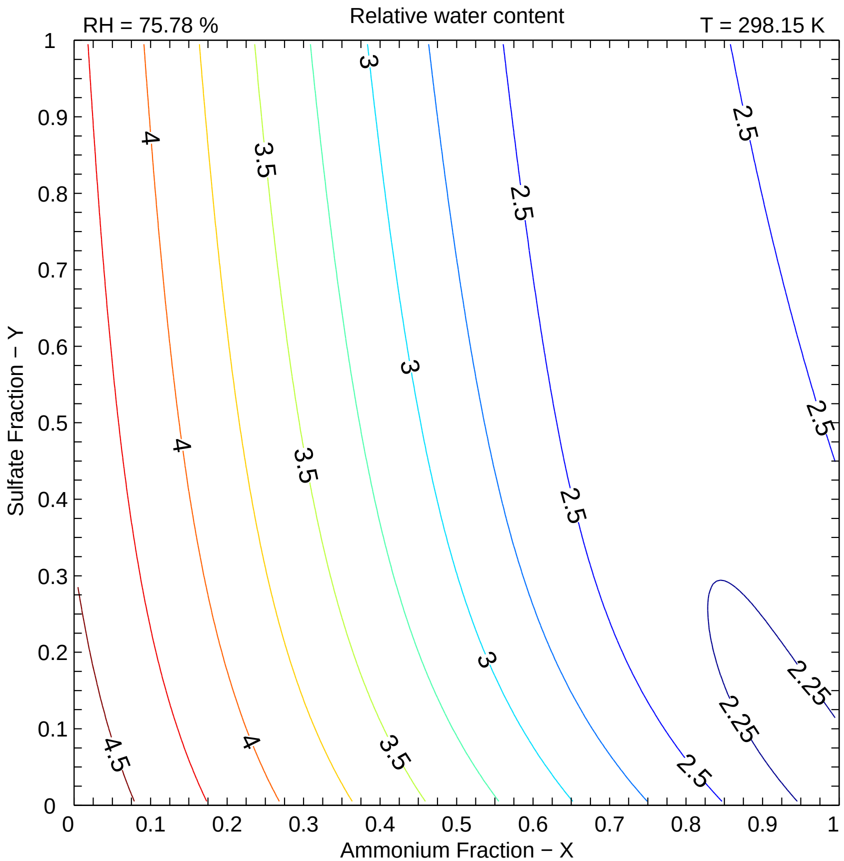
PSC model



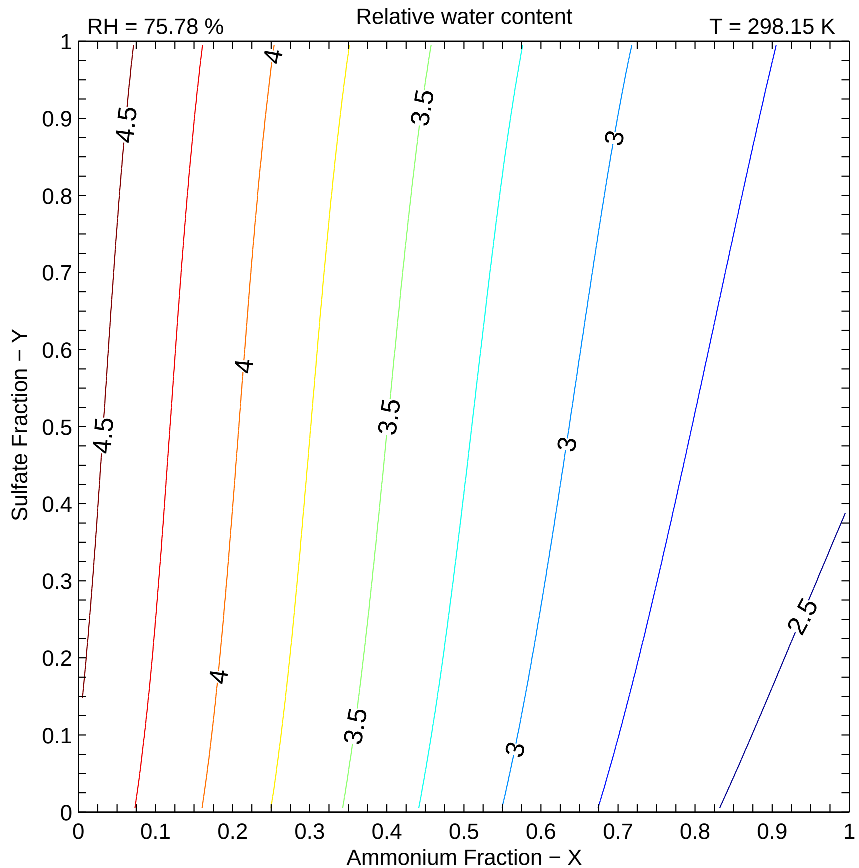
ISORROPIA model

- Isolines of water content for two models.
- Metastable equilibrium (no solid phase), open system (reverse ISORROPIA mode).

Phase diagram at $T = 298.15K$, $RH = 75.78\%$



PSC model



ExUNIQUAC model

- Isolines of water content for two models.
- Metastable equilibrium (no solid phase), open system.

Andrey Martynenko, University of Houston, andrey@math.uh.edu