Thermodynamics of Earth systems

Lecture 8:
Gibbs Free Energy, Chemical Potential and their applications (Continued)

Material covered in Lecture

Part 2: Framework

Phase Equilibria

- Gibbs phase rule: thermodynamic degrees of freedom, phases and components
- Energy in phase changes and chemical reactions

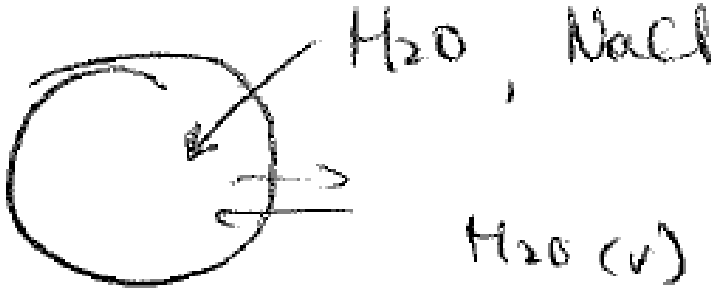
Part 3: Applications

Physical chemistry of water solutions – solution thermodynamics

- Activity and chemical potential
- Ideal solutions – Real solutions
- Equilibrium constants
- Some examples from aerosols (deliquescence and water update).
- Aerosol thermodynamic models
- The ISORROPIA-II aerosol thermodynamic model

Applications to real problems

Another example:



What is the water content of a NaCl particle in equilibrium with water vapor of a given partial pressure (relative humidity, RH)?

See "LectureNotes06.pdf"

More on the Equilibrium Constant

T-dependence of the equilibrium constant:

$$\frac{d \ln K(T)}{dT} = \frac{\Delta H^0(T)}{RT^2}$$

van't Hoff equation

Enthalpy of reaction at T

$$\Delta H^0(T) = \Delta H^0(298.15) + \Delta c_p^0 (T - 298.15)$$

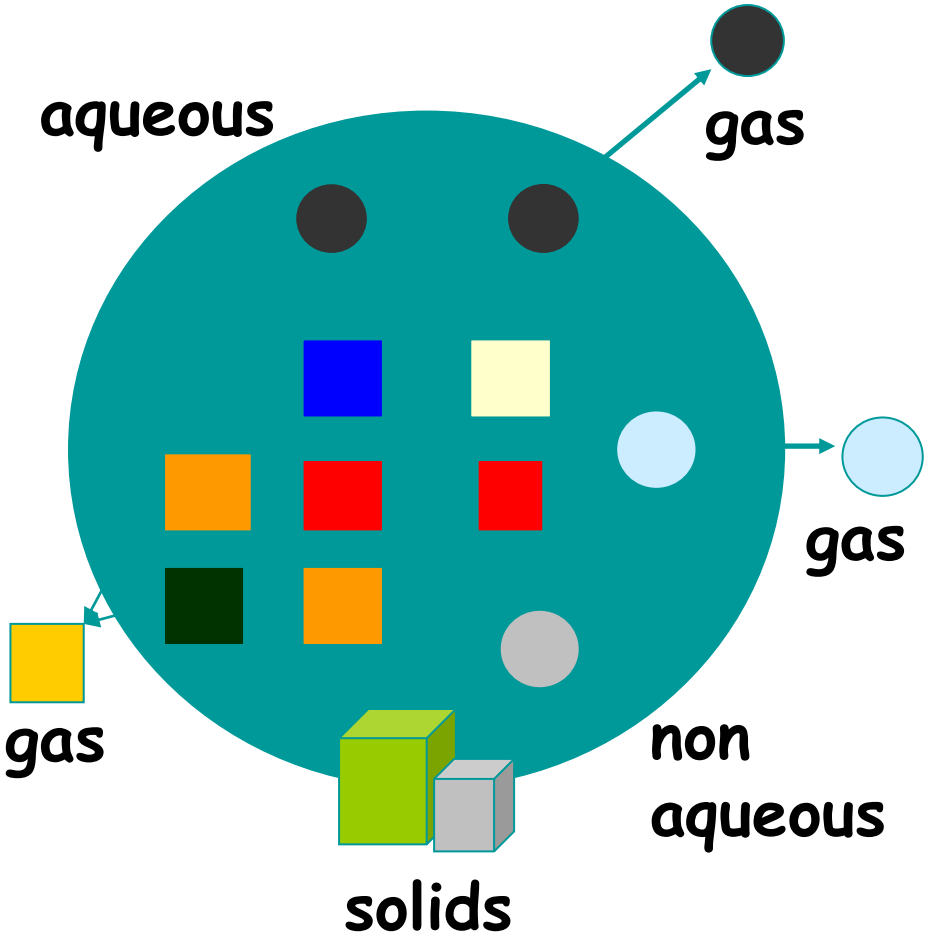
molar heat capacity of products - reactants

Substitution and integration gives:

$$K(T) = K_0 \exp\left[-\frac{\Delta H^0(T_0)}{RT_0}\left(\frac{T_0}{T} - 1\right) - \frac{\Delta c_p^0}{R}\left(1 + \ln\left(\frac{T_0}{T}\right) - \frac{T_0}{T}\right)\right]$$

where $T_o = 298.15$ K

Conceptual aerosol thermodynamic model



Assume aerosol is composed of solid, liquid and gas phases. Thermodynamic equilibrium attained when $\mathrm{d}G = 0$ (global minimum).

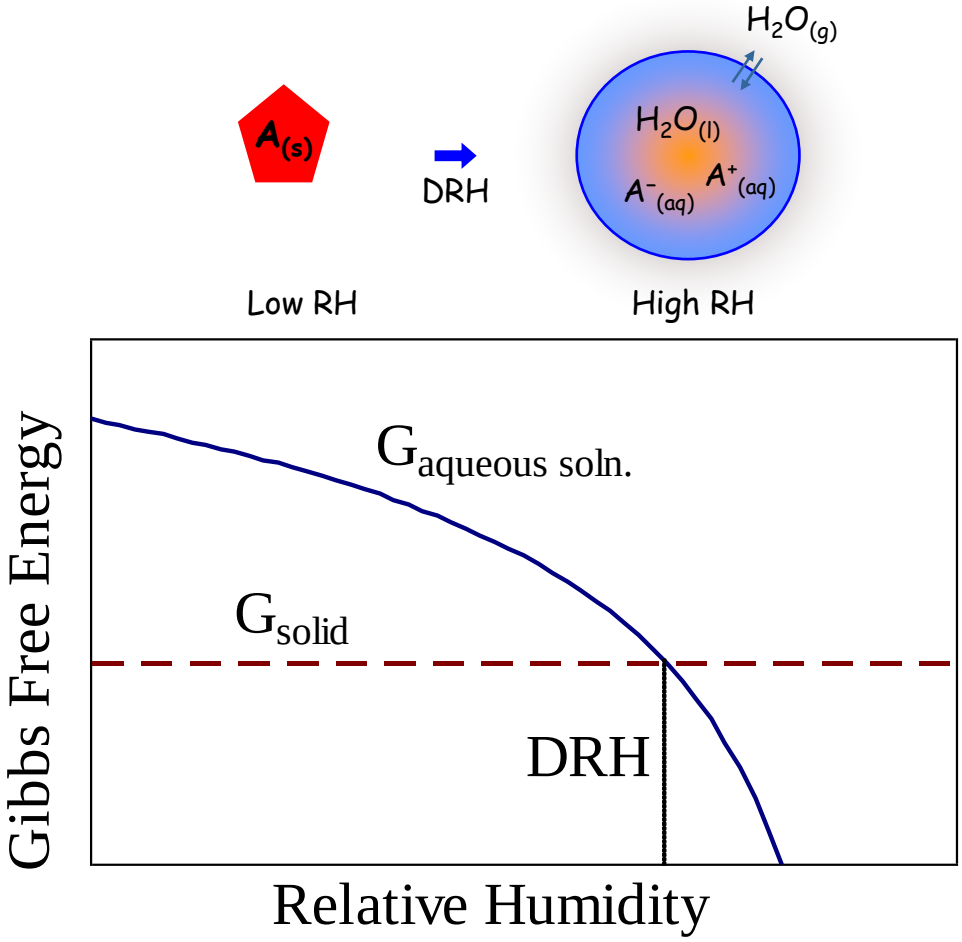
Computation of equilibrium state

Information required for obtaining thermodynamic solution:

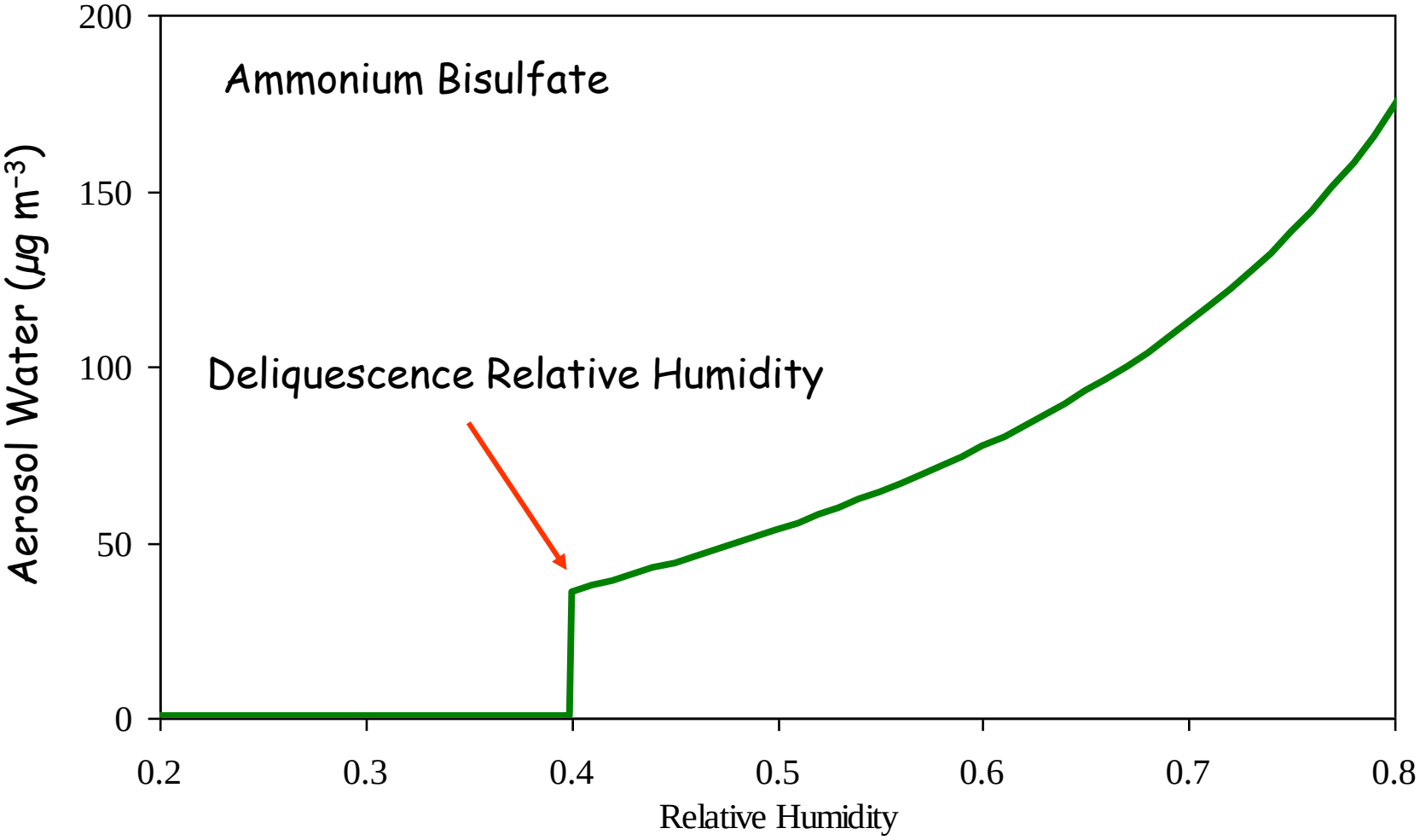
- **Vapour pressures** (for K(T))
- **Activity coefficients** (for K(T))
- **Reference chemical potentials** (for K(T))
- **Condensed phase reactions**
  (phase diagram)
- **Knowing which compounds are possible**
  (phase diagram)

Deliquescence Relative Humidity (DRH)

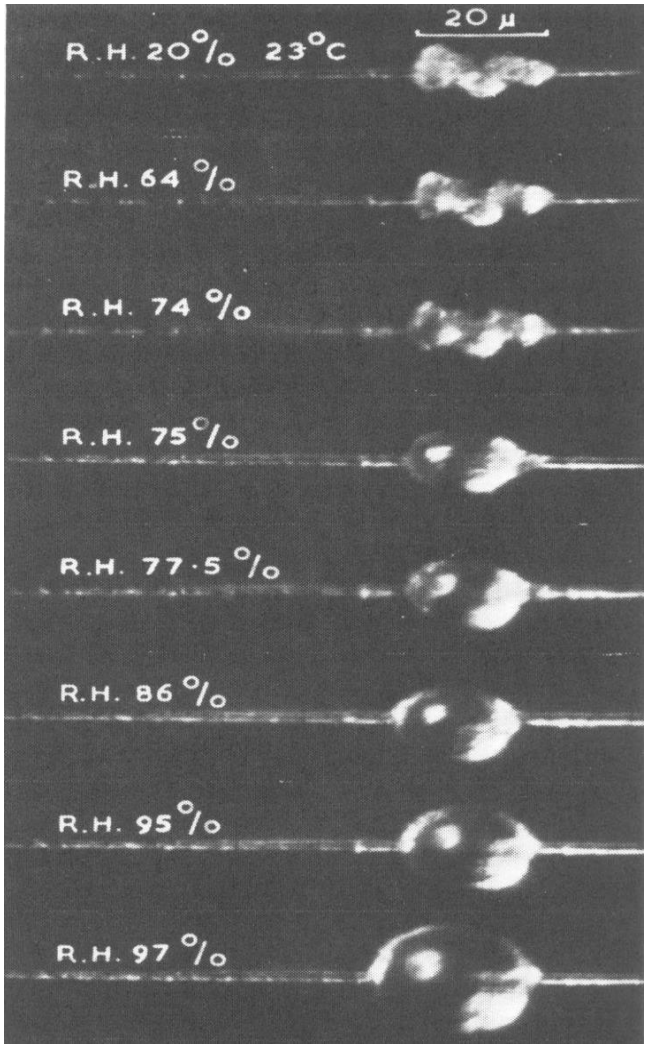
The RH at which an aerosol transitions from a solid to an aqueous solution



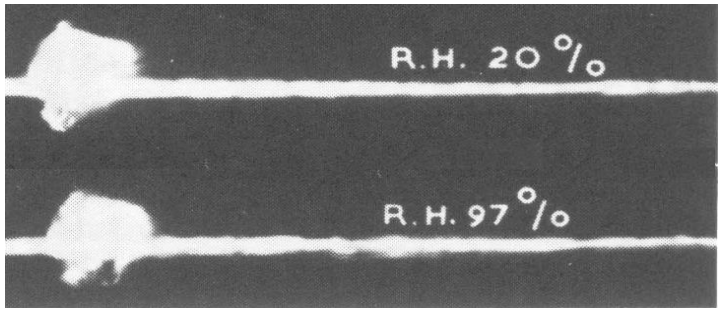
Aerosol water uptake: deliquescence



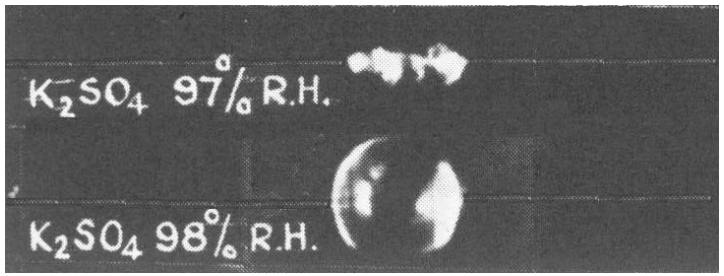
Deliquescence: Some examples



Sea Salt Particle: DRH ~ 75%



Dust Particle: no DRH

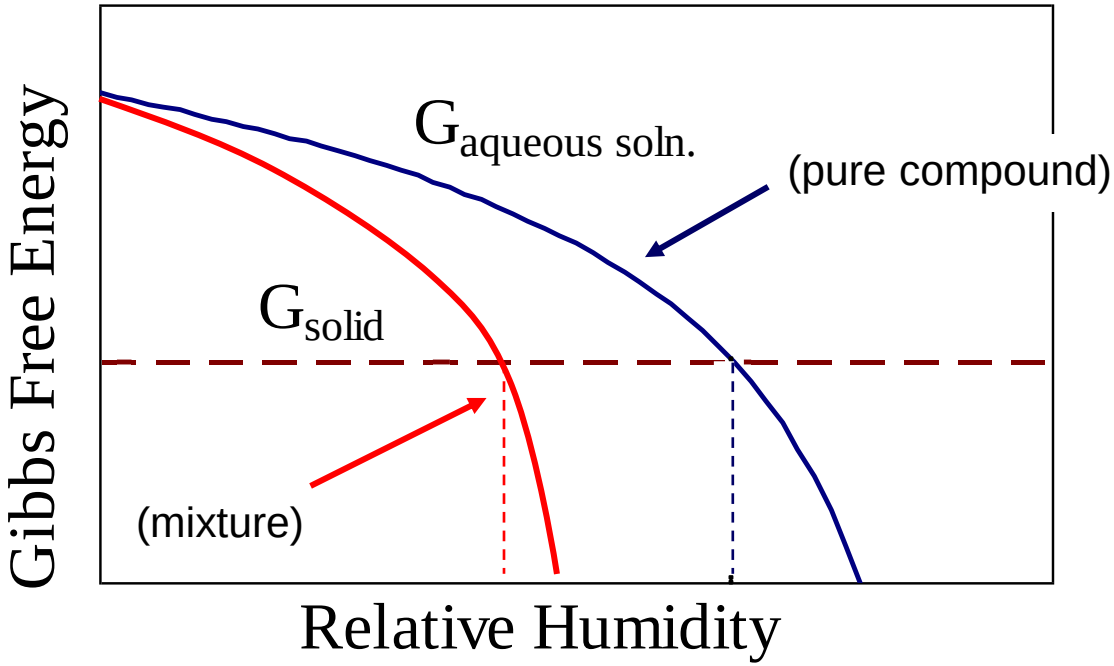


K_2SO_4 particle: DRH = 98%

Source: Twomey (1977)

Mutual Deliquescence

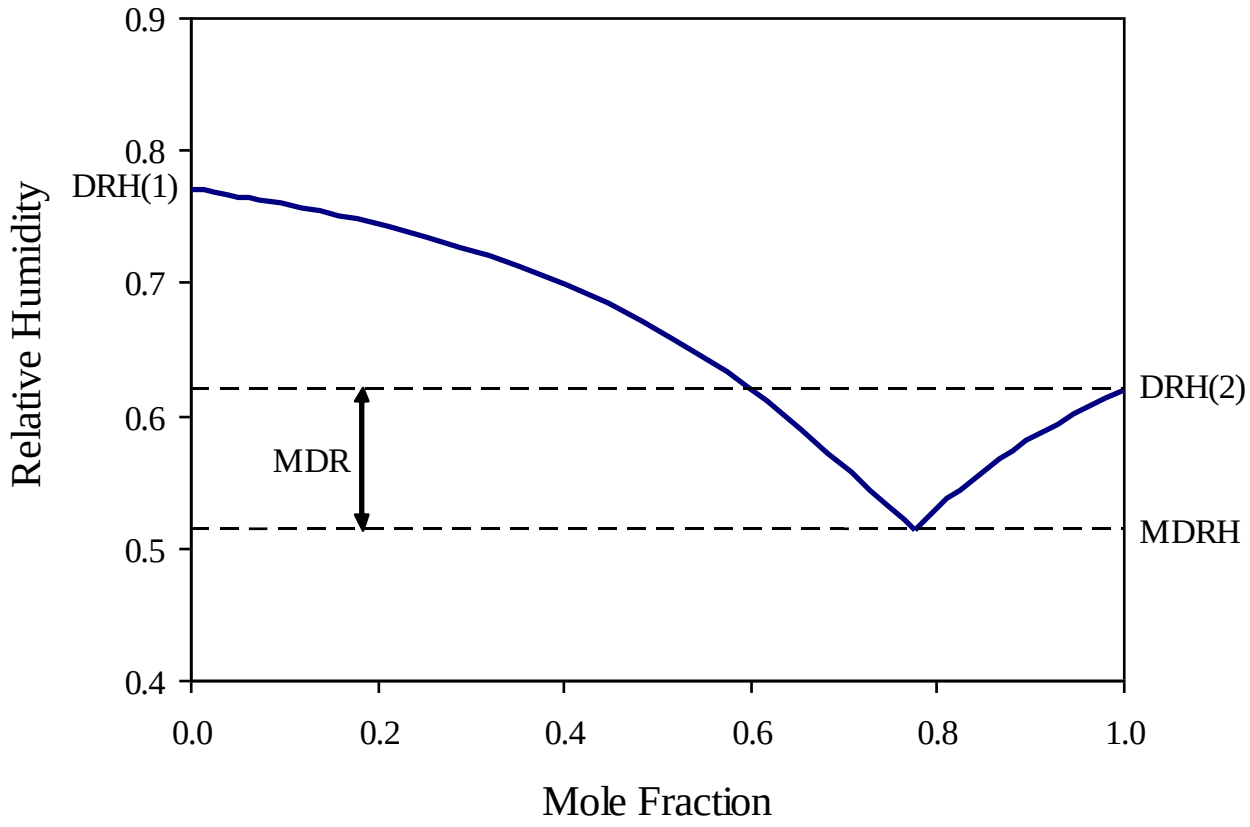
The presence of other dissolved salts tend to decrease the water activity (Gibbs Free Energy of the solution).



This means the multicomponent aerosol will deliquesce at a lower RH than the minimum DRH of each individual component.

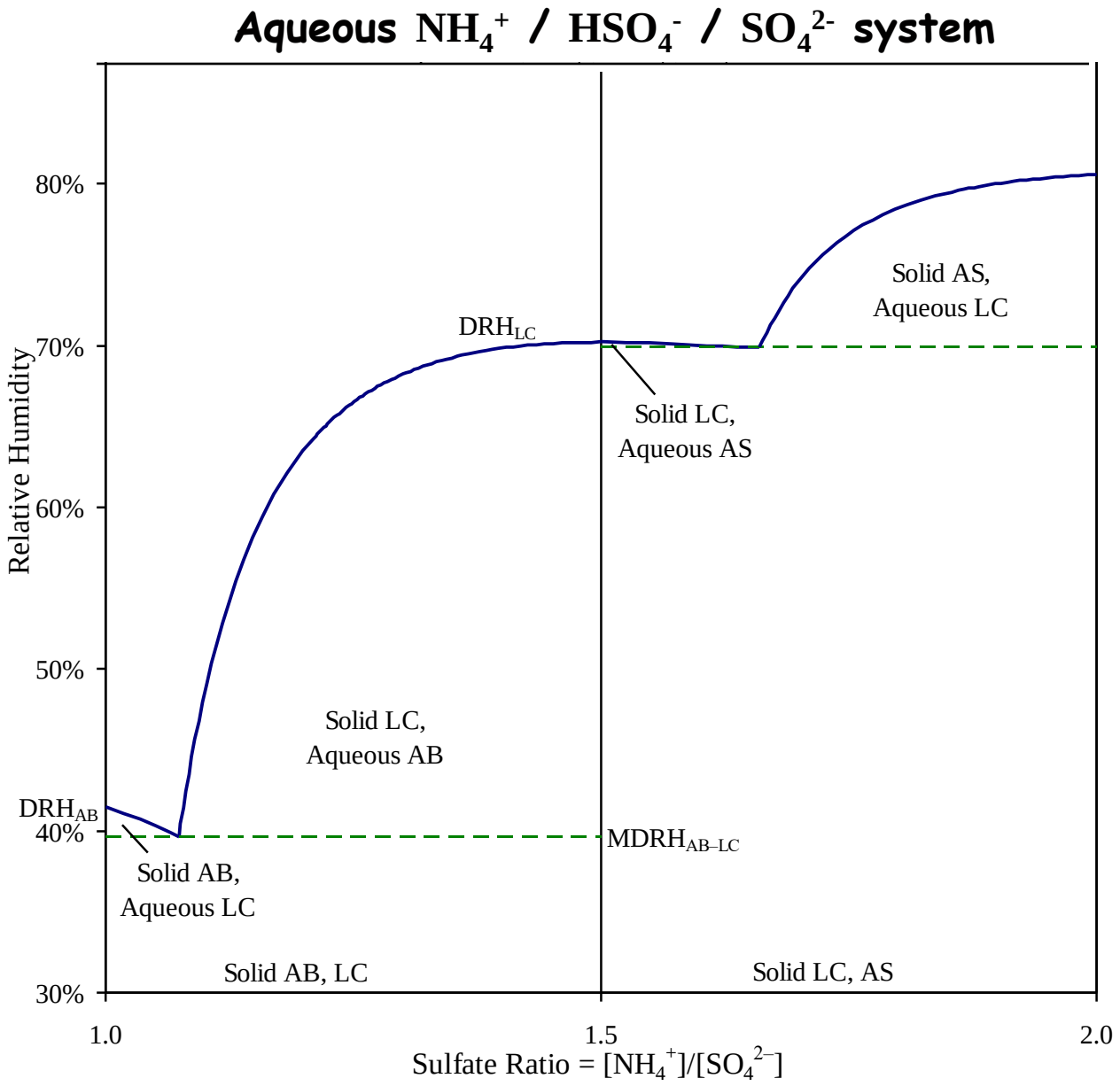
Mutual Deliquescence (Eutectic) Point

The lowest point (RH, composition) at which a fully deliquesced system can exist



The region between the MDRH and the lowest DRH of the individual salts is the Mutual Deliquescence Region

Phase Diagram: species that can coexist



Inorganic thermodynamic models

- Composition (phase diagrams) well understood
- Chemical thermodynamics well understood
- Well-established models and codes, e.g.
  - SCAPE2 (Kim *et al.*, 1993)
  - ISORROPIA (Nenes *et al.*, 1998)
  - EQUISOLV (Jacobson, 1997)
  - GFEMN (Ansari and Pandis, 1999)
  - AIM (Clegg *et al.*, 1998)
  - UH-AERO (Amundson et al., 2005)
  - MESA (Zaveri et al., 2005)

Inorganic thermodynamic models

Models differ in the:

- minimization procedure
  (direct minimization vs. chemical potent.method)
- simplifying assumptions
- the possible species in each phase
  (phase diagram)
- calculation method for ionic interactions
  (activity coefficients)
- COMPUTATIONAL SPEED.

Inorganic thermo models: classification

- **Direct minimization of Gibbs free energy (e.g.,AIM)**
  - requires search of entire domain to accommodate multiple local minima
  - robust but often computationally intensive
- **Chemical potential method using knowledge of aerosol system behavior (e.g.,ISORROPIA)**
  - Reduces the number of equations and variables to be solved.
  - Constrained equilibrium equations may be solved or simplified numerically.
  - Faster, but requires additional subroutines to be written for each new chemical species.

Recall:Equilibrium by direct minimization

Objective:minimize $G = G_{solids} + G_{gases} + G_{salts} + G_{water}$

$$\begin{cases} G_{solids} = \sum_i n_i \mu_i^0 \\ G_{gases} = \sum_i n_i \mu_i^0 + RT\left[\sum_i n_i \ln(p_i)\right] \\ G_{salts} = \sum_i n_i \mu_i^0 + RT\left[\sum_i n_i \ln(m_i) + \sum_{salt} n_{salt} \ln\left(\gamma_{salt}^x\right)\right] \\ G_{water} = n_{water}\left[\mu_{water}^0 + RT \ln\left(\frac{RH}{100}\right)\right] \end{cases}$$

With constraints of mass and charge conservation

Recall: Chemical potential method

Start from "generic" chemical reaction

$$a\mathrm{A} + b\mathrm{B} \longleftrightarrow c\mathrm{C} + d\mathrm{D}$$

Statement of chemical equilibrium

$$\sum_i \nu_i \mu_i = 0 \qquad \text{where} \qquad \mu_i = \mu_i^0(T) + RT \ln a_i$$

Expanding chemical potentials gives $\sum_i \nu_i \mu_i^0 + RT \sum_i \nu_i \ln a_i = 0$

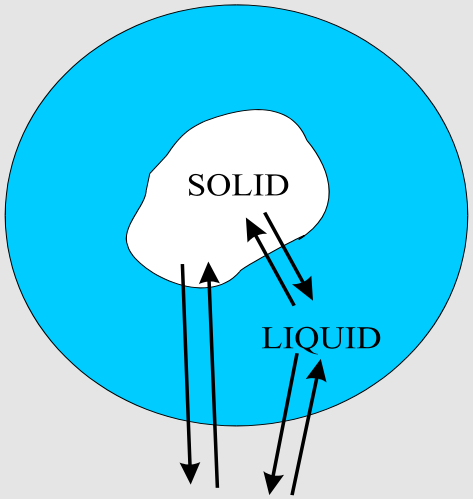
After some rearrangement:

$$\frac{a_D^d a_C^c}{a_A^a a_B^b} = \exp\left(-\frac{d\nu_D + c\nu_C - a\nu_A - b\nu_B}{RT} \right)$$

Equilibrium constant $K(T)$

"ISORROPIA" models (Fountoukis and Nenes, 2007)

Solid phase: $NaHSO_4$, NH_4HSO_4 , Na_2SO_4 , NaCl, $(NH_4)_2SO_4$, $(NH_4)_3H(SO_4)_2$, NH_4NO_3, NH_4Cl, $NaNO_3$, **K_2SO_4, $KHSO_4$, KNO_3, KCl, $CaSO_4$, $Ca(NO_3)_2$, $CaCl_2$, $MgSO_4$, $MgCl_2$, $Mg(NO_3)_2$**



Liquid phase: Na^+, NH_4^+, H^+, OH^-, HSO_4^-, SO_4^{2-}, NO_3^-, Cl^-, H_2O, $HNO_{3(aq)}$, $HCl_{(aq)}$, $NH_{3(aq)}$, **Ca^{2+}, K^+, Mg^{2+}**

Gas phase: HNO_3, HCl, NH_3, H_2O

Species in **bold** were introduced in ISORROPIA II (Fountoukis and Nenes, 2007)

http://nenes.eas.gatech.edu/ISORROPIA

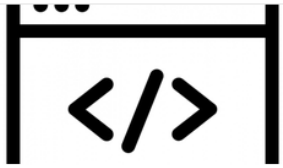
ISORROPIA

ISORROPIA was originally developed at the Division of Marine and Atmospheric Chemistry of the Rosenstiel School of Marine and Atmospheric Science, University of Miami, and ISORROPIA II at the Schools of Earth & Atmospheric Sciences and Chemical & Biomolecular Engineering at the Georgia Institute of Technology.

The objective was to develop a computationally efficienct and rigorous aerosol thermodynamics module for use in regional and global aerosol models.
The complete theory of ISORROPIA, together with a detailed description of the equations solved, the activity coefficient calculation methods and the computational algorithms used can be found in Nenes et al., 1998a,b and Fountoukis and Nenes, 2007. The performance and advantages of ISORROPIA over the usage of other thermodynamic equilibrium codes has been assessed in numerous studies (e.g., Nenes et al. 1998b; Ansari and Pandis, 1999ab; Yu et al., 2005). It has been evaluated wth numerous in-situ data sets (e.g., Yu et al., 2005; Nowak et al., 2006; Fountoukis et al., 2009)

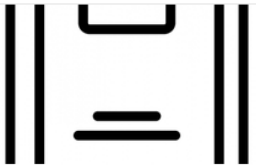
Model Description

See more



Code Repository

See more



User's Manual

See more

http://isorropia.epfl.ch

The "ISORROPIA" models Nenes *et al.*, 1998; Fountoukis and Nenes, 2007; Kakavas et al., 2023)

- Adopted by numerous modeling groups throughout the world.
- Urban-scale air quality models, chemical transport and global circulation models

Examples:

- NASA GISS Global Climate Model
- EPA Community Air Quality model (CMAQ)
- Georgia Tech SAMI model
- EPRI's CAMx model
- UAM-AERO
- Meteo-France Group
- Max Planck Institute for Tropospheric Research
- University of Athens, Greece
- Ford Motors - Aachen

The "ISORROPIA" models (Nenes *et al.*, 1998; Fountoukis and Nenes, 2007)

Some reactions…

$$HSO_{4(aq)}^{-} \xleftrightarrow{K_1} H_{(aq)}^{+} + SO_{4(aq)}^{2-}$$

$$NH_{3(g)} \xleftrightarrow{K_{21}} NH_{3(aq)}$$

$$NH_{3(aq)} + H_2O_{(aq)} \xleftrightarrow{K_{22}} NH_{4(aq)}^{+} + OH_{(aq)}^{-}$$

$$HCl_{(g)} \xleftrightarrow{K_3} H_{(aq)}^{+} + Cl_{(aq)}^{-}$$

$$HNO_{3(g)} \xleftrightarrow{K_4} H_{(aq)}^{+} + NO_{3(aq)}^{-}$$

$$Na_2SO_{4(s)} \xleftrightarrow{K_5} 2Na_{(aq)}^{+} + SO_{4(aq)}^{2-}$$

$$NH_4Cl_{(s)} \xleftrightarrow{K_6} NH_{3(g)} + HCl_{(g)}$$

$$(NH_4)_2SO_{4(s)} \xleftrightarrow{K_7} 2NH_{4(aq)}^{+} + SO_{4(aq)}^{2-}$$

$$NaHSO_{4(s)} \xleftrightarrow{K_{11}} Na_{(aq)}^{+} + HSO_{4(aq)}^{-}$$

$$NH_4HSO_{4(s)} \xleftrightarrow{K_{12}} NH_{4(aq)}^{+} + HSO_{4(aq)}^{-}$$

$$(NH_4)_3H(SO_4)_{2(s)} \xleftrightarrow{K_{13}} 3NH_{4(aq)}^{+} + HSO_{4(aq)}^{-} + SO_{4(aq)}^{2-}$$

$$H_2O_{(aq)} \xleftrightarrow{K_w} H_{(aq)}^{+} + OH_{(aq)}^{-}$$

$$NaCl_{(s)} \xleftrightarrow{K_8} Na_{(aq)}^{+} + Cl_{(aq)}^{-}$$

$$NaNO_{3(s)} \xleftrightarrow{K_9} Na_{(aq)}^{+} + NO_{3(aq)}^{-}$$

$$NH_4NO_{3(s)} \xleftrightarrow{K_{10}} NH_{3(g)} + HNO_{3(g)}$$

The "ISORROPIA" models (Nenes *et al.*, 1998; Fountoukis and Nenes, 2007)

More reactions…

Reaction	Equilibrium Constant Expression
$Ca(NO_3)_{2(s)} \leftrightarrow Ca^{2+}_{(aq)} + 2NO^{-}_{3(aq)}$	$[Ca^{2+}][NO_3^-]^2 \gamma_{Ca^{2+}} \gamma^2_{NO_3^-}$
$CaCl_{2(s)} \leftrightarrow Ca^{2+}_{(aq)} + 2Cl^{-}_{(aq)}$	$[Ca^{2+}][Cl^-]^2 \gamma_{Ca^{2+}} \gamma^2_{Cl^-}$
$K_2SO_{4(s)} \leftrightarrow 2K^{+}_{(aq)} + SO^{2-}_{4(aq)}$	$[K^+]^2 [SO_4^{2-}] \gamma^2_{K^+} \gamma_{SO_4^{2-}}$
$KHSO_{4(s)} \leftrightarrow K^{+}_{(aq)} + HSO^{-}_{4(aq)}$	$[K^+][HSO_4^-] \gamma_{K^+} \gamma_{HSO_4^-}$
$KNO_{3(s)} \leftrightarrow K^{+}_{(aq)} + NO^{-}_{3(aq)}$	$[K^+][NO_3^-] \gamma_{K^+} \gamma_{NO_3^-}$
$KCl_{(s)} \leftrightarrow K^{+}_{(aq)} + Cl^{-}_{(aq)}$	$[K^+][Cl^-] \gamma_{K^+} \gamma_{Cl^-}$
$MgSO_{4(s)} \leftrightarrow Mg^{2+}_{(aq)} + SO^{2-}_{4(aq)}$	$[Mg^{2+}][SO_4^{2-}] \gamma_{Mg^{2+}} \gamma_{SO_4^{2-}}$
$Mg(NO_3)_{2(s)} \leftrightarrow Mg^{2+}_{(aq)} + 2NO^{-}_{3(aq)}$	$[Mg^{2+}][NO_3^-]^2 \gamma_{Mg^{2+}} \gamma^2_{NO_3^-}$
$MgCl_{2(s)} \leftrightarrow Mg^{2+}_{(aq)} + 2Cl^{-}_{(aq)}$	$[Mg^{2+}][Cl^-]^2 \gamma_{Mg^{2+}} \gamma^2_{Cl^-}$

Phase Diagram /ISORROPIA subroutines

Division of the whole aerosol species regime into subdomains based on the following molar ratios:

$$R_{SO_4} = \frac{[NH_4^+] + [Ca^{2+}] + [K^+] + [Mg^{2+}] + [Na^+]}{[SO_4^{2-}]}$$

Sulfate ratio

$$R_{(Cr+Na)} = \frac{[Ca^{2+}] + [K^+] + [Mg^{2+}] + [Na^+]}{[SO_4^{2-}]}$$

Crustal + Na ratio

$$R_{Cr} = \frac{[Ca^{2+}] + [K^+] + [Mg^{2+}]}{[SO_4^{2-}]}$$

Crustal ratio

ISORROPIA: Solving for Equilibrium

- Sulfate Ratios determine what salts are possible
- RH determines possible phases (solid, liquid, or both)
- Solve system of equations:
  - *Equilibrium reactions*
  - *Conservation of mass*
  - *Conservation of charge (electroneutrality)*
- Activity coefficients iterated (Bisection method)

"ISORROPIA" models: Solution Methodology

Five types of composition regimes are defined:

- $R_{SO_4} < 1$: Sulfate super-rich

Solid species: NH_4HSO_4, $NaHSO_4$, $KHSO_4$, $CaSO_4$

- $1 \le R_{SO_4} < 2$: Sulfate rich

Solid species: NH_4HSO_4, $NaHSO_4$, $KHSO_4$, $CaSO_4$, K_2SO_4, $MgSO_4$, $(NH_4)_2SO_4$, Na_2SO_4, $(NH_4)_3H(SO_4)_2$

- $R_{SO_4} > 2$, $R_{(Cr+Na)} < 2$: Sulfate poor, Crustal + Na rich

Solid species: $CaSO_4$, K_2SO_4, $MgSO_4$, $(NH_4)_2SO_4$, Na_2SO_4, NH_4NO_3, NH_4Cl

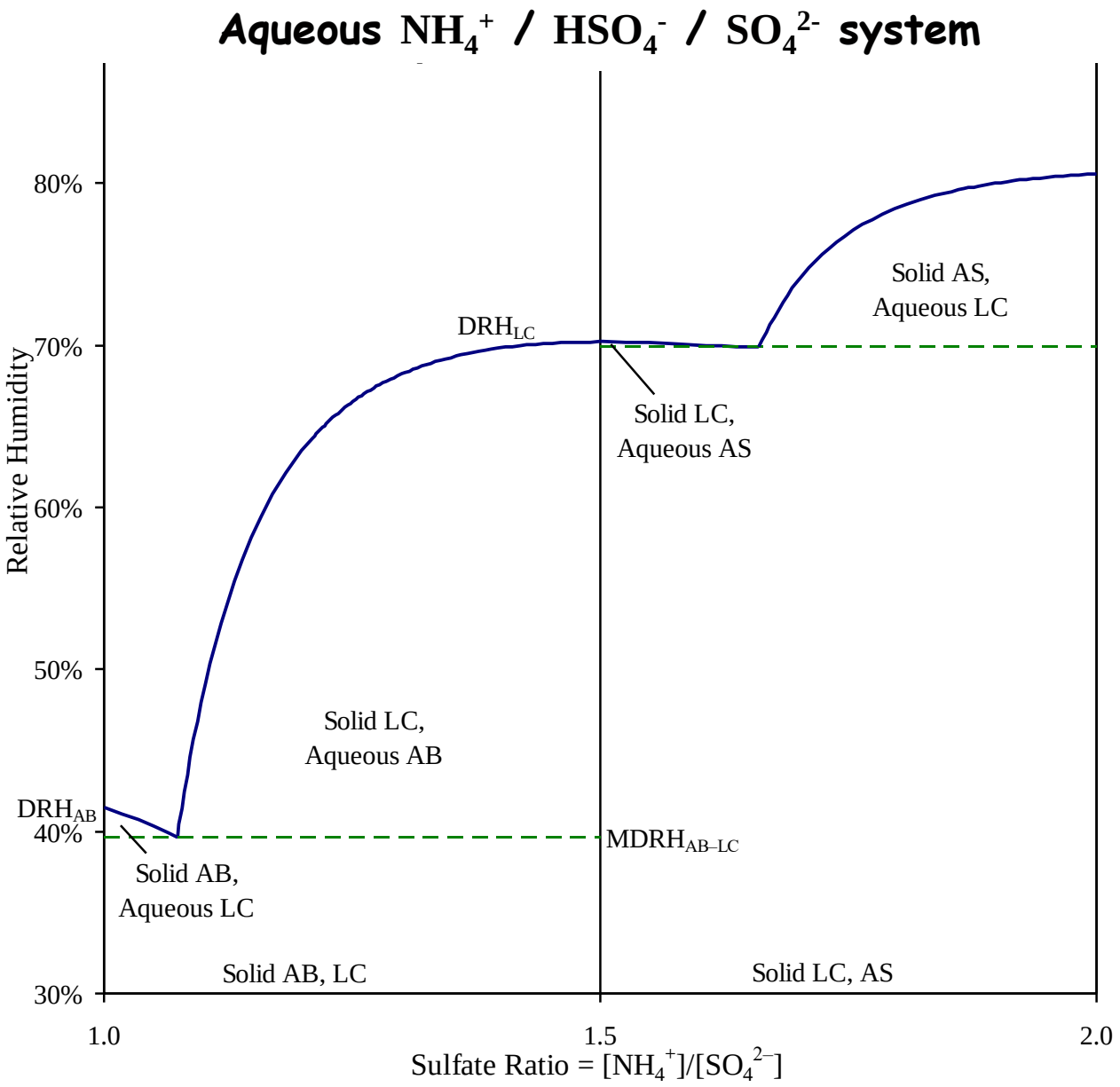
- $R_{SO_4} > 2$, $R_{(Cr+Na)} > 2$, $R_{Cr} < 2$: Sulfate poor, Cr + Na rich, Cr poor

Solid species: $CaSO_4$, K_2SO_4, $MgSO_4$, Na_2SO_4, NH_4NO_3, NH_4Cl, $NaNO_3$, $NaCl$

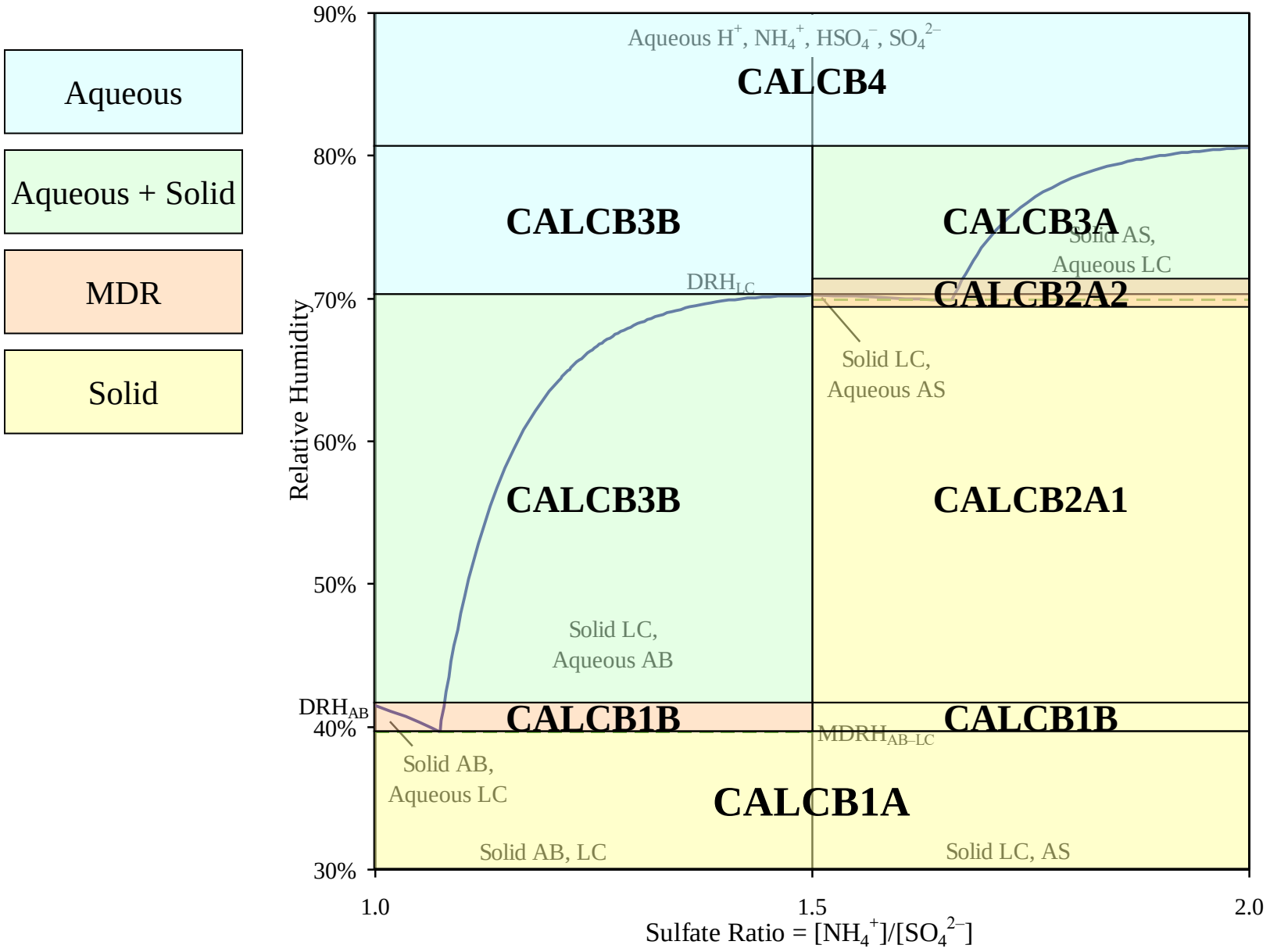
- $R_{SO_4} > 2$, $R_{(Cr+Na)} > 2$, $R_{Cr} > 2$: Sulfate poor, Cr + Na rich, Cr rich

Solid species: $CaSO_4$, K_2SO_4, $MgSO_4$, NH_4NO_3, NH_4Cl, $NaNO_3$, $NaCl$, $Ca(NO_3)_2$, $CaCl_2$, KNO_3, KCl, $Mg(NO_3)_2$, $MgCl_2$

Phase Diagram (ISORROPIA-II subroutine map)

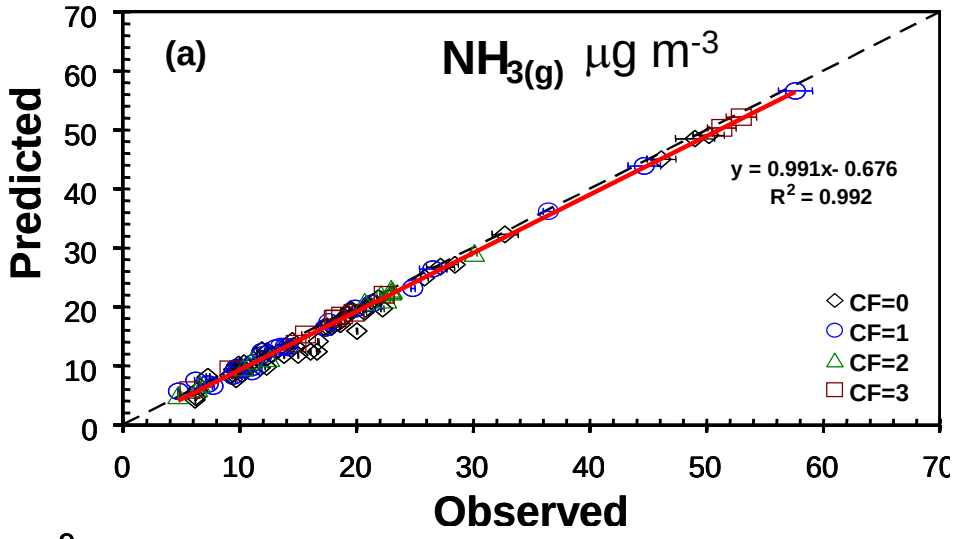


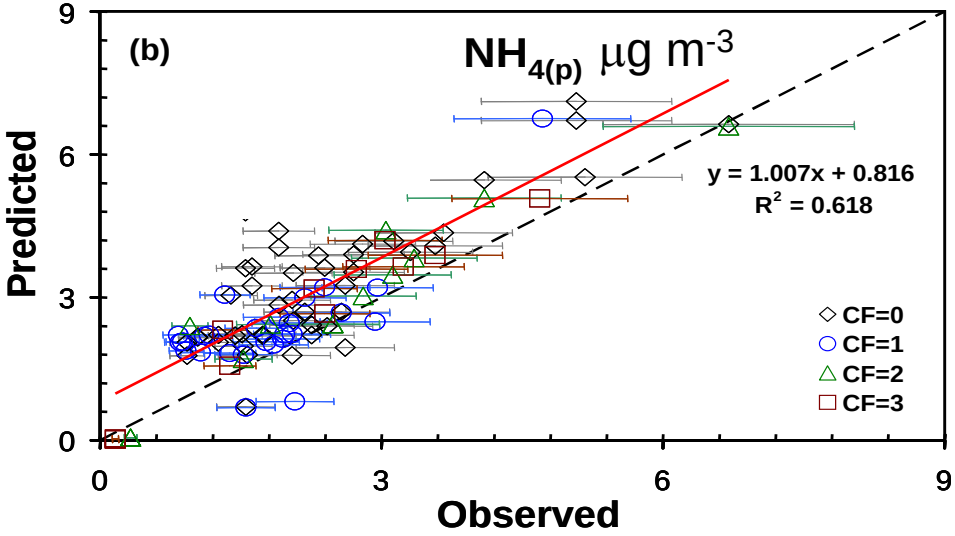
Phase Diagram (ISORROPIA-II subroutine map)



Models: comparison with data

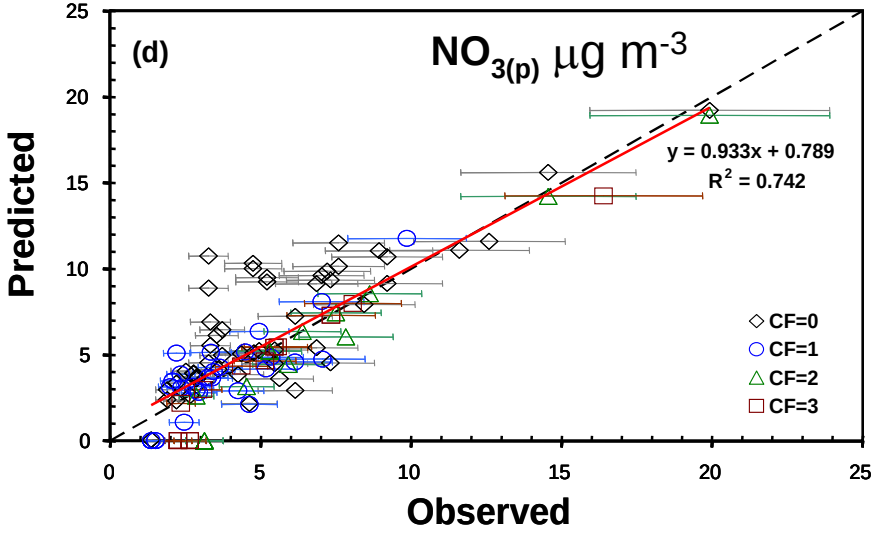
Mexico City MILAGRO Experiment; March 2006





Particulate NH_4 predicted to within 20%

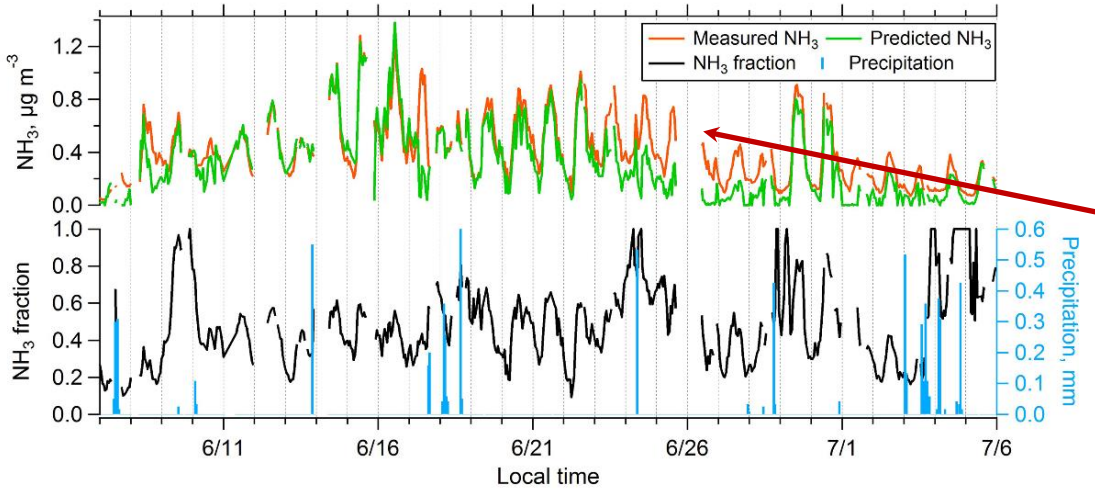
Particulate NO_3 predicted to within 10%



Fountoukis et al, ACP (2009)

Models: comparison with data

SOAS: *(Southern Oxidant Aerosol Study)* 6/7, 2013 Centreville, AL (CTR)



Guo et al., ACP, 2015.

Comparison of predicted vs. observed gas-phase NH_3.