

Overhead Slides for
Chapter 18, Part 2
of
Fundamentals of
Atmospheric Modeling

by

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Solvation and Hydration

Solvation

Bonding between solvent and solute in solution

Hydration

- When solvent is liquid water, solvation is hydration
- Hydration of cations --> lone pairs of electrons on oxygen atom of water attach to cations
- Hydration of anions --> water molecule attaches to anion via hydrogen bonding

Water Equation

Quantify amount of hydration with empirical water equation

Zdanovskii-Stokes-Robinson (ZSR) equation

Example with two species, x and y

$$\frac{\mathbf{m}_{x,m}}{\mathbf{m}_{x,a}} + \frac{\mathbf{m}_{y,m}}{\mathbf{m}_{y,a}} = 1 \quad (18.64)$$

$\mathbf{m}_{x,a}$, $\mathbf{m}_{y,a}$ = molalities of x and y , alone in solution at given relative humidity

$\mathbf{m}_{x,m}$, $\mathbf{m}_{y,m}$ = molalities of x and y , when mixed together, at same relative humidity

Table 18.3. ZSR equation predictions for a sucrose (species a) - mannitol (species b) mixture at two different water activities. Data from Stokes and Robinson (1966).

$\mathbf{m}_{x,a}$	$\mathbf{m}_{y,a}$	$\mathbf{m}_{x,m}$	$\mathbf{m}_{y,m}$	$\frac{\mathbf{m}_{x,m}}{\mathbf{m}_{x,a}} + \frac{\mathbf{m}_{y,m}}{\mathbf{m}_{y,a}}$
0.7751	0.8197	0.6227	0.1604	0.9990
0.9393	1.0046	0.1900	0.8014	1.0000

Water Equation

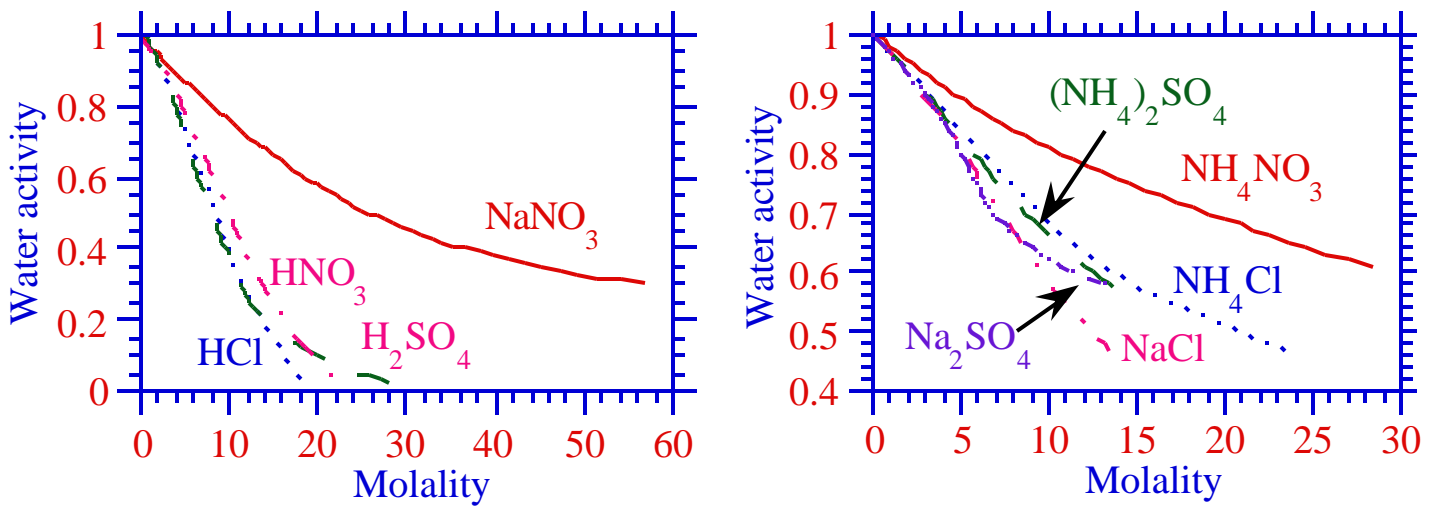
Generalized ZSR equation

$$\frac{\mathbf{m}_{k,m}}{\mathbf{m}_{k,a}} = 1 \quad (18.65)$$

Polynomial expression for molality of electrolyte alone in solution at a given water activity

$$\mathbf{m}_{k,a} = Y_{0,k} + Y_{1,k}a_w + Y_{2,k}a_w^2 + Y_{3,k}a_w^3 + \dots \quad (18.66)$$

Figure 18.3. Water activities of several electrolytes at 298.15 K



Temperature Dependence of Water Activity

Temperature dependence of binary water activity coefficients under ambient surface conditions is small.

Temperature dependence of water activity

$$\ln a_w(T) = \ln a_w^0 - \frac{m_v \mathbf{m}_{k,a}^2}{1000R^*} \frac{T_L}{T_0} \frac{L}{\mathbf{m}_{k,a}} + T_C \frac{c_P}{\mathbf{m}_{k,a}} \quad (18.67)$$

Polynomial for water activity at reference temperature

$$\ln a_w^0 = A_0 + A_1 \mathbf{m}_{k,a}^{1/2} + A_2 \mathbf{m}_{k,a} + A_3 \mathbf{m}_{k,a}^{3/2} + \dots \quad (18.68)$$

Combine (18.67), (18.68), (18.54)

$$\ln a_w(T) = A_0 + A_1 \mathbf{m}_{k,a}^{1/2} + A_2 \mathbf{m}_{k,a} + E_3 \mathbf{m}_{k,a}^{3/2} + E_4 \mathbf{m}_{k,a}^2 + \dots \quad (18.69)$$

$$E_l = A_l - \frac{0.5(l-2)m_v}{1000R^*} \frac{T_L}{T_0} U_{l-2} + T_C V_{l-2} \quad I = 3, \dots \quad (18.70)$$

Example

	\mathbf{m}_{HCl}	= 16 m
	T	= 273 K
---	a_w	= 0.09
	T	= 310 K
---	a_w	= 0.11

Practical Use of Water Equation

Rearrange (18.65)

$$c_w = \frac{1000}{m_v} \sum_{i=1}^{N_C} \sum_{j=1}^{N_A} \frac{c_{i,j,m}}{\mathbf{m}_{i,j,a}} \quad (18.71)$$

$\mathbf{m}_{i,j,a}$ = binary molalities of species alone in solution

$c_{i,j,m}$ = hypothetical mole cm^{-3} of electrolyte pair when mixed in solution with all other components

In a model, ion concentrations known but hypothetical electrolyte concentrations unknown --> find hypothetical concentrations

Example 18.1.

6 $\mu\text{moles m}^{-3}$ of H^+

6 $\mu\text{moles m}^{-3}$ Na^+

7 $\mu\text{moles m}^{-3}$ of Cl^-

5 $\mu\text{moles m}^{-3}$ of NO_3^-

Combine ions in a way to satisfy mass balance constraints:

$$c_{\text{H}^+,m} = c_{\text{HNO}_3,m} + c_{\text{HCl},m}$$

$$c_{\text{Na}^+,m} = c_{\text{NaNO}_3,m} + c_{\text{NaCl},m}$$

$$c_{\text{Cl}^-,m} = c_{\text{HCl},m} + c_{\text{NaCl},m}$$

$$c_{\text{NO}_3^-,m} = c_{\text{HNO}_3,m} + c_{\text{NaNO}_3,m}$$

Practical Use of Water Equation

Table 18.4. Three sets of electrolytes concentrations that satisfy mass balance constraints of example.

	$c_{\text{HCl},m}$	$c_{\text{HNO}_3,m}$	$c_{\text{NaCl},m}$	$c_{\text{NaNO}_3,m}$
Case 1	6	0	1	5
Case 2	4	2	3	3
Case 3	1	5	6	0

Automatic method to recombine ions into hypothetical electrolytes

Execute the following three equations, in succession, for each undissociated electrolyte, i,j

$$\text{Electrolyte} \quad c_{i,j,m} = \min \frac{c_{i,m}}{i}, \frac{c_{j,m}}{j} \quad (18.72)$$

$$\text{Cation} \quad c_{i,m} = c_{i,m} - i c_{i,j,m}$$

$$\text{Anion} \quad c_{j,m} = c_{j,m} - j c_{i,j,m}$$

Result corresponds to case 1 in table (18.4) for the example

Example Equilibrium Problem

Consider two equilibrium reactions



For equilibrium concentrations, solve
equilibrium constant equations
mass balance equations
charge balance equation
water equation
with Newton-Raphson iteration

Equilibrium constant equations

$$\frac{\mathbf{m}_{\text{H}^+,eq} \mathbf{m}_{\text{Cl}^-,eq}^2}{p_{\text{HCl},s,eq}} = K_{eq}(T) \quad (18.74)$$

$$\frac{\mathbf{m}_{\text{H}^+,eq} \mathbf{m}_{\text{SO}_4^{2-},eq}^3}{\mathbf{m}_{\text{HSO}_4^-,eq} \mathbf{m}_{\text{H}^+,\text{HSO}_4^-,eq}^2} = K_{eq}(T)$$

Mass balance equations

$$C_{\text{HCl(g),eq}} + c_{\text{Cl}^-,eq} = C_{\text{HCl(g),t-h}} + c_{\text{Cl}^-,t-h} \quad (18.75)$$

$$c_{\text{HSO}_4^-,eq} + c_{\text{SO}_4^{2-},eq} = c_{\text{HSO}_4^-,t-h} + c_{\text{SO}_4^{2-},t-h} \quad (18.76)$$

Example Equilibrium Problem

Surface vapor pressure as a function of mole concentration

$$p_{\text{HCl},s,eq} = C_{\text{HCl}(g),s,eq} R^* T \quad (18.77)$$

Molality as a function of mole concentration

$$\mathbf{m}_{\text{Cl}^-,eq} = \frac{1000c_{\text{Cl}^-,eq}}{c_{w,eq}m_v}$$

Charge balance equation

$$c_{\text{Cl}^-,eq} + c_{\text{HSO}_4^-,eq} + 2c_{\text{SO}_4^{2-},eq} = c_{\text{H}^+,eq} \quad (18.78)$$

Water equation

$$c_{w,eq} = \frac{1000}{m_w} \frac{c_{\text{H}^+, \text{Cl}^-, m}}{\mathbf{m}_{\text{H}^+, \text{Cl}^-, a}} + \frac{c_{\text{H}^+, \text{HSO}_4^-, m}}{\mathbf{m}_{\text{H}^+, \text{HSO}_4^-, a}} + \frac{c_{2\text{H}^+, \text{SO}_4^{2-}, m}}{\mathbf{m}_{2\text{H}^+, \text{SO}_4^{2-}, a}} \quad (18.79)$$

Hypothetical mole concentration constraints

$$c_{\text{H}^+,eq} = c_{\text{H}^+, \text{Cl}^-, m} + c_{\text{H}^+, \text{HSO}_4^-, m} + 2c_{2\text{H}^+, \text{SO}_4^{2-}, m} \quad (18.80)$$

$$c_{\text{Cl}^-,eq} = c_{\text{H}^+, \text{Cl}^-, m}$$

$$c_{\text{HSO}_4^-,eq} = c_{\text{H}^+, \text{HSO}_4^-, m}$$

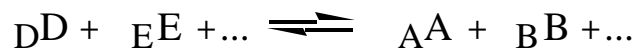
$$c_{\text{SO}_4^{2-},eq} = c_{2\text{H}^+, \text{SO}_4^{2-}, m}$$

Mass-Flux Iterative Method

- Initialize species concentrations so that charge is conserved
- No intelligent first guess required
- Solution mass and charge conserving and always converges

Solution method for one equilibrium equation

Example equilibrium equation and coefficient relation



$$\frac{\{A\}^A \{B\}^B \dots}{\{D\}^D \{E\}^E \dots} = K_{eq}(T)$$

1) Calculate smallest ratio of mole concentration to moles in denominator and numerator, respectively

$$Q_d = \min \frac{C_{D,1}}{D}, \frac{C_{E,1}}{E} \quad (18.81)$$

$$Q_n = \min \frac{c_{A,1}}{A}, \frac{c_{B,1}}{B}$$

2) Initialize two parameters

$$z_1 = 0.5(Q_d + Q_n)$$

$$x_1 = Q_d - z_1.$$

Mass-Flux Iterative Method

Add or subtract mass flux factor (x) to mole concentrations

$$c_{A,l+1} = c_{A,l} + A \ x_l \quad c_{B,l+1} = c_{B,l} + B \ x_l \quad (18.82)$$

$$c_{D,l+1} = c_{D,l} - D \ x_l \quad c_{E,l+1} = c_{E,l} - E \ x_l$$

3) Compare ratio of activities to equilibrium constant

$$F = \frac{m_{A,l+1}^A m_{B,l+1}^B}{p_{D,l+1}^D p_{E,l+1}^E} \frac{1}{K_{eq}(T)} \quad (18.83)$$

4) Cut z in half

$$z_{l+1} = 0.5z_l$$

5) Check convergence

$$\begin{array}{ll}
 > 1 & x_{l+1} = -z_{l+1} \\
 F = < 1 & x_{l+1} = +z_{l+1} \\
 = 1 & \text{convergence}
 \end{array} \quad (18.84)$$

Return to (18.82) until convergence occurs

Deliquescence Relative Humidity

Deliquescence

Process by which a particle takes up liquid water, lowering its surface vapor pressure

Deliquescence relative humidity (DRH)

The relative humidity at which an initially-dry solid first takes on liquid water during an increase in relative humidity. Above the DRH, the solid may not exist.

Crystallization relative humidity (CRH)

The relative humidity at which an initially-supersaturated aqueous electrolyte becomes crystalline upon a decrease in relative humidity.

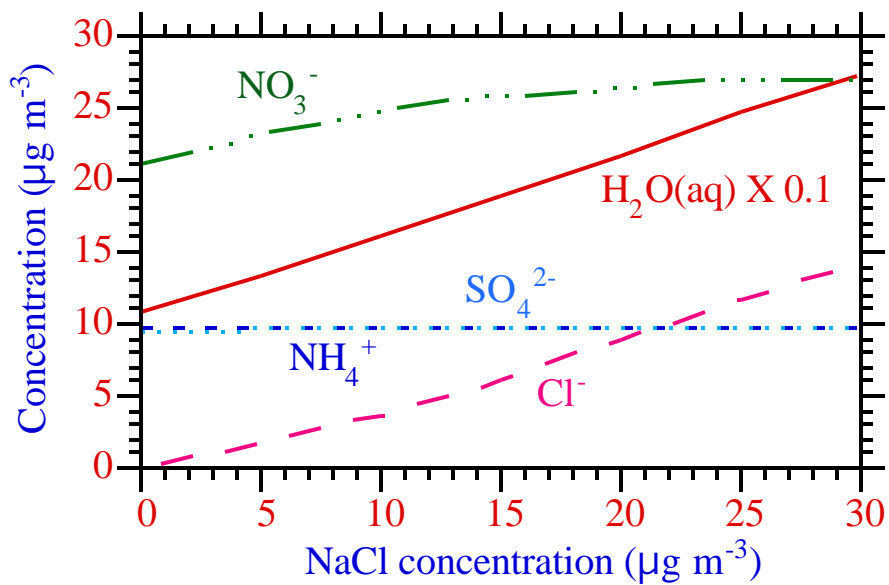
Table 18.9. DRHs and CRHs for several electrolytes at 298 K

Electrolyte	DRH (percent)	CRH (percent)	Electrolyte	DRH (percent)	CRH (percent)
NaCl	75.28	47	(NH ₄) ₂ SO ₄	79.97	37-40
Na ₂ SO ₄	84.2	57-59	NH ₄ HSO ₄	40.0	0.05-22
NaHSO ₄	52.0	<0.05	NH ₄ NO ₃	61.83	25-32
NaNO ₃	74.5	0.05-30	(NH ₄) ₃ H(SO ₄) ₂	69	35-44
NH ₄ Cl	77.1	47	KCl	84.26	62

In a mixture, the DRH of a solid in equilibrium with the solution is lower than the DRH of the solid alone

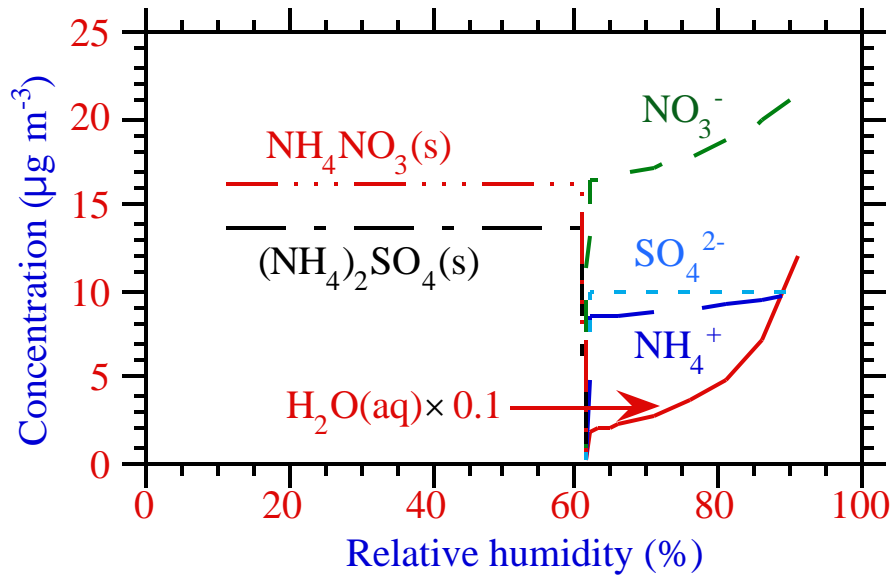
Equilibrium Solver Results

Fig. 18.4. Aerosol composition versus NaCl concentration when the relative humidity was 90%. Other initial conditions were $\text{H}_2\text{SO}_4(\text{aq}) = 10 \mu\text{g m}^{-3}$, $\text{HCl}(\text{g}) = 0 \mu\text{g m}^{-3}$, $\text{NH}_3(\text{g}) = 10 \mu\text{g m}^{-3}$, $\text{HNO}_3(\text{g}) = 30 \mu\text{g m}^{-3}$, and $T = 298 \text{ K}$.



Equilibrium Solver Results

Fig. 18.5. Aerosol composition versus relative humidity. Initial conditions were $\text{H}_2\text{SO}_4(\text{aq}) = 10 \mu\text{g m}^{-3}$, $\text{HCl}(\text{g}) = 0 \mu\text{g m}^{-3}$, $\text{NH}_3(\text{g}) = 10 \mu\text{g m}^{-3}$, $\text{HNO}_3(\text{g}) = 30 \mu\text{g m}^{-3}$, and $T = 298 \text{ K}$.



Dissolutional Growth

Saturation vapor pressure of nitric acid

$$p_{q,s,i} = \frac{\mathbf{m}_{q,i}}{H_q} \quad (18.87)$$

Saturation vapor pressure as function of gas mole concentration

$$p_{q,s,i} = C_{q,s,i} 1000 R^* T \quad (18.88)$$

Molality as function of particle mole concentration

$$\mathbf{m}_{q,i} = \frac{1000 c_{q,i}}{m_v c_{w,i}} \quad (18.89)$$

Substitute (8.87) and (8.89) into (8.88)

$$C_{q,s,i} = \frac{p_{q,s,i}}{1000 R^* T} = \frac{\mathbf{m}_{q,i}}{1000 R^* T H_q} = \frac{c_{q,i}}{m_v c_{w,i} R^* T H_q} = \frac{c_{q,i}}{H_{q,i}} \quad (18.90)$$

where

$$H_{q,i} = m_v c_{w,i} R^* T H_q$$

Dissolutional Growth

Condensational growth equations

$$\frac{dc_{q,i,t}}{dt} = k_{q,i,t-h} (C_{q,t} - S_{q,i,t-h} C_{q,s,i,t-h}) \quad (17.65)$$

$$\frac{dC_{q,t}}{dt} = - \sum_{i=1}^{N_B} \left[k_{q,i,t-h} (C_{q,t} - S_{q,i,t-h} C_{q,s,i,t-h}) \right] \quad (17.66)$$

Substitute (18.90) and equilibrium terms

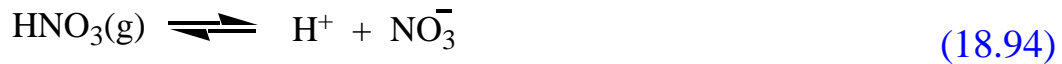
--> Dissolutional growth equations

$$\frac{dc_{q,i,t}}{dt}_{ge,eq} = k_{q,i,t-h} C_{q,t} - S_{q,i,t-h} \frac{c_{q,i,t}}{H_{q,i,t-h}} + \frac{dc_{q,i,t}}{dt}_{eq} \quad (18.91)$$

$$\frac{dC_{q,t}}{dt} = - \sum_{i=1}^{N_B} \left[k_{q,i,t-h} C_{q,t} - S_{q,i,t-h} \frac{c_{q,i,t}}{H_{q,i,t-h}} \right] \quad (18.92)$$

Dissolution of Strong Acids or Bases

Equilibrium expressions



Equilibrium coefficient expressions

$$\frac{\mathbf{m}_{\text{H}^+,i} \mathbf{m}_{\text{Cl}^-,i}^2}{p_{\text{HCl(g)},s,i}} = K_{\text{HCl}} \quad (18.93)$$

$$\frac{\mathbf{m}_{\text{H}^+,i} \mathbf{m}_{\text{NO}_3^-,i}^2}{p_{\text{HNO}_3(\text{g}),s,i}} = K_{\text{HNO}_3} \quad (18.94)$$

$$\frac{\mathbf{m}_{\text{NH}_4^+,i}}{p_{\text{NH}_3(\text{g}),s,i} \mathbf{m}_{\text{H}^+,i}} = K_{\text{NH}_3} \quad (18.95)$$

Dissolution of Strong Acids/Bases

Ammonium / hydrogen ion activity coefficient relationship

$$\frac{i, \text{NH}_4^+}{i, \text{H}^+} = \frac{i, \text{NH}_4^+ i, \text{NO}_3^-}{i, \text{H}^+ i, \text{NO}_3^-} = \frac{2}{i, \text{H}^+ / \text{NO}_3^-} = \frac{i, \text{NH}_4^+ i, \text{Cl}^-}{i, \text{H}^+ i, \text{Cl}^-} = \frac{2}{i, \text{H}^+ / \text{Cl}^-} \quad (18.97)$$

Combine (18.93) - (18.95) with (18.88) and (18.89)

$$C_{\text{Cl}^-,s,i} = \frac{p_{\text{Cl}^-,s,i}}{1000 R^* T} = \frac{\mathbf{m}_{\text{H}^+,i} \mathbf{m}_{\text{Cl}^-,i} \frac{2}{i, \text{H}^+ / \text{Cl}^-}}{1000 R^* T K_{\text{HCl}}} = \frac{c_{\text{Cl}^-,i} \mathbf{m}_{\text{H}^+,i} \frac{2}{i, \text{H}^+ / \text{Cl}^-}}{m_{\text{v}} c_{\text{w},i} R^* T K_{\text{HCl}}} = \frac{c_{\text{Cl}^-,i}}{H_{\text{Cl}^-,i}} \quad (18.98)$$

$$\begin{aligned} C_{\text{NO}_3^-,s,i} &= \frac{p_{\text{NO}_3^-,s,i}}{1000 R^* T} = \frac{\mathbf{m}_{\text{H}^+,i} \mathbf{m}_{\text{NO}_3^-,i} \frac{2}{i, \text{H}^+ / \text{NO}_3^-}}{1000 R^* T K_{\text{HNO}_3}} \\ &= \frac{c_{\text{NO}_3^-,i} \mathbf{m}_{\text{H}^+,i} \frac{2}{i, \text{H}^+ / \text{NO}_3^-}}{m_{\text{v}} c_{\text{w},i} R^* T K_{\text{HNO}_3}} = \frac{c_{\text{NO}_3^-,i}}{H_{\text{NO}_3^-,i}} \end{aligned} \quad (18.99)$$

$$\begin{aligned} C_{\text{NH}_4^+,s,i} &= \frac{p_{\text{NH}_4^+,s,i}}{1000 R^* T} = \frac{\mathbf{m}_{\text{NH}_4^+,i} i, \text{NH}_4^+}{\mathbf{m}_{\text{H}^+,i} i, \text{H}^+ 1000 R^* T K_{\text{NH}_3}} \\ &= \frac{c_{\text{NH}_4^+,i} i, \text{NH}_4^+}{\mathbf{m}_{\text{H}^+,i} i, \text{H}^+ m_{\text{v}} c_{\text{w},i} R^* T K_{\text{NH}_3}} = \frac{c_{\text{NH}_4^+,i}}{H_{\text{NH}_4^+,i}} \end{aligned} \quad (18.100)$$

Dissolution of Strong Acids/Bases

$$\frac{dc_{Cl^-},i}{dt} = k_{HCl,i} C_{HCl} - S_{Cl^-},i \frac{c_{Cl^-},i}{H_{Cl^-},i} + \frac{dc_{Cl^-},i}{dt} \quad eq \quad (18.104)$$

$$\frac{dc_{NO_3^-},i}{dt} = k_{HNO_3,i} C_{HNO_3} - S_{NO_3^-},i \frac{c_{NO_3^-},i}{H_{NO_3^-},i} + \frac{dc_{NO_3^-},i}{dt} \quad eq \quad (18.105)$$

$$\frac{dc_{NH_4^+},i}{dt} = k_{NH_3,i} C_{NH_3} - S_{NH_4^+},i \frac{c_{NH_4^+},i}{H_{NH_4^+},i} + \frac{dc_{NH_4^+},i}{dt} \quad eq \quad (18.106)$$

where

$$H_{Cl^-},i = \frac{m_{v,c_w,i} R^* T K_{HCl}}{\mathbf{m}_{H^+,i} \quad i,H^+/Cl^-} \quad (18.101)$$

$$H_{NO_3^-},i = \frac{m_{v,c_w,i} R^* T K_{HNO_3}}{\mathbf{m}_{H^+,i} \quad i,H^+/NO_3^-} \quad (18.102)$$

$$H_{NH_4^+},i = \frac{\mathbf{m}_{H^+,i} \quad i,H^+ m_{v,c_w,i} R^* T K_{NH_3}}{i,NH_4^+} \quad (18.103)$$

Analytical Predictor of Dissolution

Integrate (18.91) for final aerosol concentration

$$c_{q,i,t} = \frac{H_{q,i,t-h} C_{q,t}}{S_{q,i,t-h}} + c_{q,i,t-h} - \frac{H_{q,i,t-h} C_{q,t}}{S_{q,i,t-h}} \exp - \frac{h S_{q,i,t-h} k_{q,i,t-h}}{H_{q,i,t-h}} \quad (18.110)$$

Mass balance equation

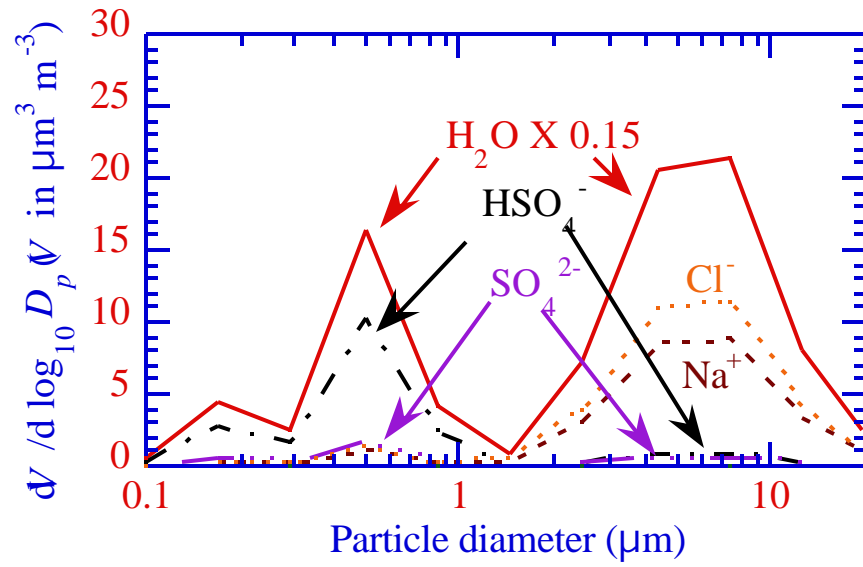
$$C_{q,t} + \sum_{i=1}^{N_B} (c_{q,i,t}) = C_{q,t-h} + \sum_{i=1}^{N_B} (c_{q,i,t-h}) = C_{tot} \quad (18.111)$$

Substitute (18.110) into (18.111)

$$C_{q,t} = \frac{C_{q,t-h} + \sum_{i=1}^{N_B} c_{q,i,t-h} \left[1 - \exp - \frac{h S_{q,i,t-h} k_{q,i,t-h}}{H_{q,i,t-h}} \right]}{1 + \sum_{i=1}^{N_B} \frac{H_{q,i,t-h}}{S_{i,q,t-h}} \left[1 - \exp - \frac{h S_{q,i,t-h} k_{q,i,t-h}}{H_{q,i,t-h}} \right]} \quad (18.112)$$

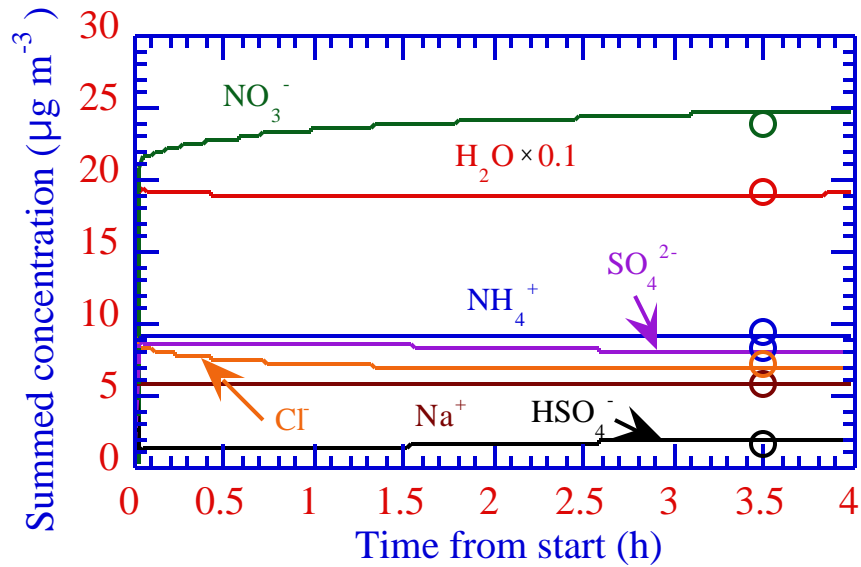
Simulations

Fig. 18.6. Initial distribution, $f_r = 90\%$ and $T = 298\text{ K}$



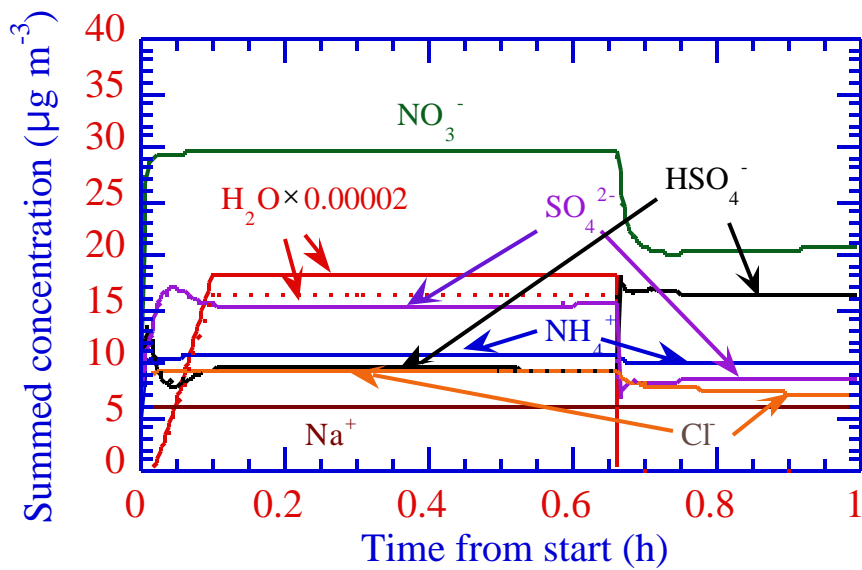
Simulations

Fig. 18.7. APD / MFI vs. SMVGEAR / MFI results when 1-s interval was used. $f_r = 90\%$, $T = 298$ K.



Simulations

Fig. 18.8. APD / APC / MFI vs. SMVGEAR / MFI results when 10-s interval was used. At time zero, the relative humidity was increased from 90% to 100.001%. The r. h. was then reset to 100.001% after every 10 s growth calculation for the first five minutes, at which point it was no longer reset. After forty minutes, the relative humidity was reduced back to 90% to simulate evaporation.



Simulations

Fig. 18.9. Model size distribution initially, after growth, and after evaporation obtained from the simulation shown in fig. 8.8.

