Numerical Techniques to Solve Condensational and Dissolutional Growth Equations When Growth is Coupled to Reversible Reactions

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ABSTRACT. Noniterative, unconditionally stable numerical techniques for solving condensational and dissolutional growth equations are given. Growth solutions are compared to Gear-code solutions for three cases when growth is coupled to reversible equilibrium chemistry. In all cases, results from the new growth schemes matched Gear-code solutions nearly exactly when growth and equilibrium calculations were operator-split with a 1 s time interval. Results also matched well for a 15 s interval. With a 15 s interval, the growth-equilibrium schemes can be used in a three-dimensional model. Longer operator splitting intervals, in some cases, induced oscillations in concentrations caused by delays in feedback between equilibrium and growth calculations. Simulation results indicated that gases and aerosols were closer to equilibrium when the relative humidity was 90% than when it was 40%.


INTRODUCTION
Among the processes affecting the size distribution and composition of atmospheric aerosols and cloud drops are condensation, dissolution, and evaporation. Several numerical methods have been developed to simulate condensation and evaporation. These include finite element methods (e.g., Varoglu and Finn, 1980; Tsang and Brock, 1986; Tsang and Huang, 1990), discrete size bin methods (e.g., Gelbard and Seinfeld, 1980; Toon et al., 1988; Rao and McMurry, 1989), the cubic spline method (e.g., Middleton and Brock, 1976), modified upwind difference methods (e.g., Smolarkiewicz, 1983; Tsang and Korgaonkar, 1987), and moments methods (e.g., Friedlander, 1983; Whitby, 1985; Lee, 1985; Brock et al., 1986). Dissolution and evaporation in dilute solutions have also been simulated in a number of papers (e.g., Schwartz, 1984; Chameides, 1984; Jacob, 1986; Pandis and Seinfeld, 1989; Bott and Carmichael, 1993; Sande et al., 1995). One paper proposed a model that simulates dissolution and evaporation in concentrated solutions (Wexler and Seinfeld, 1991).

Numerical studies of aerosols require that growth and chemistry equations be solved at high ionic strengths. Only the last paper listed above considered growth in aerosols at high ionic strengths, but results were not reported for three dimensions. Because aerosols affect spatial gas and radiative fields, their simulation in three-dimensions is important. In this paper, noniterative, unconditionally stable solutions to condensational and dissolutional growth equations
are given. Both schemes are computationally fast; yet, to simulate aerosol growth at high ionic strengths, they must be coupled to an equilibrium solver, which is slower. The coupled growth/equilibrium model discussed is still fast enough to be used in three dimensions. Predictions from the model are compared to those from a coupled ordinary differential equation solver/equilibrium scheme for three cases.

**GROWTH EQUATIONS**

An equation describing condensational growth of a component $q$ onto particles of size $i$ and subsequent reversible reaction is

$$
\frac{dc_{q,i}}{dt} = k_{q,i} \left(C_q - S_{q,i} c_{q,i} \right) + \left( \frac{dc_{q,i}}{dt} \right)_{eq}
$$

(1)

(Jacobson, 1997a), where $c_{q,i}$ is the mole concentration of species $q$ in size bin $i$ (moles cm$^{-3}$ air), $C_q$ is the ambient vapor mole concentration of species $q$ in the gas phase (moles cm$^{-3}$ air), $c_{q,i}$ is the surface vapor mole concentration of a condensing species over a flat surface (moles cm$^{-3}$ air), $k_{q,i}$ is the mass transfer rate between the gas phase and all particles of size $i$ (s$^{-1}$), $S_{q,i}$ is the saturation ratio at equilibrium, and $\left( \frac{dc_{q,i}}{dt} \right)_{eq}$ is the rate of change in particle concentration of the species due to reversible equilibrium reactions (e.g., dissociation, precipitation, etc.).

The mass transfer rate in Eq. (1) can be approximated as $k_{q,i} = n_i \pi r_i D_{q,i}^{eff}$, where $n_i$ is the number concentration of particles of size $i$ (partic. cm$^{-3}$), $r_i$ is the fluctuating radius of a single particle, and $D_{q,i}^{eff}$ is an effective diffusion coefficient (cm$^2$ s$^{-1}$) that accounts for the geometry of vapor collision with small particles and ventilation of heat and vapor during sedimentation of large particles containing liquid water. One expression for $D_{q,i}^{eff}$ is given in Jacobson and Turco (1995).

For condensational growth, $c_{q,i}$ is often parameterized empirically or calculated from the Clausius–Clapeyron equation. For dissolutional and surface reaction growth, $c_{q,i}$ is a function of particle composition. The surface vapor concentration of a soluble, nondissociating species over a dilute solution is

$$
c_{q,i} = \frac{m_{q,i}}{1000 R^* TH_q} = \frac{c_{q,i}}{m_w c_{w,i} R^* TH_q} = \frac{c_{q,i}}{H'_{q,i}}
$$

(2)

where $m_{q,i} = 1000 c_{q,i}/m_w c_{w,i}$ is the molality of species $q$ in solution (mole kg$^{-1}$), $R^*$ is the ideal gas constant (L atm mole$^{-1}$ K$^{-1}$), $T$ is temperature (K), $H_q$ is the Henry’s constant of the species (moles kg$^{-1}$ atm$^{-1}$), $c_{q,i}$ is the mole concentration of dissolved gas $q$ in size bin $i$ (moles cm$^{-3}$ air), $c_{w,i}$ is the mole concentration of liquid water in size bin $i$, $m_w$ is the molecular weight of water (g mole$^{-1}$), and $H'_{q,i} = m_w c_{w,i} R^* TH_q$. Substituting Eq. (2) into Eq. (1) gives

$$
\frac{dc_{q,i}}{dt} = k_{q,i} \left(C_q - S_{q,i} \frac{c_{q,i}}{H'_{q,i}} \right) + \left( \frac{dc_{q,i}}{dt} \right)_{eq},
$$

(3)

which is the rate of change of $c_{q,i}$ due to dissolutional growth/evaporation.

When strong acids or bases dissolve in solution, they dissociate. Hydrochloric acid (HCl) and ammonia (NH$_3$) dissociate to H$^+$/Cl$^-$ and NH$_4^+$/OH$^-$, respectively. In such cases, $H'_{q,i}$ in Eq. (3) can be replaced with

$$
H'_{Cl^{-},i} = \frac{m_w c_{w,i} R^* TK_{HCl}}{m_{H^+} \gamma_{H^+/Cl^-}},
$$

(4)

$$
H'_{NH_4^+,i} = \frac{m_{H^+} \gamma_{H^+/NH_4^+} m_w c_{w,i} R^* TK_{NH_3}}{\gamma_{i,NH_4^+}},
$$

(5)

respectively. In Eqs. (4) and (5), the $K$’s are equilibrium coefficients of the reactions, HCl(g) $\leftrightarrow$ H$^+$ + Cl$^-$ and NH$_3$(g) + H$^+$ $\leftrightarrow$ NH$_4^+$, respectively. In Eq. (4), $\gamma$ is an activity coefficient of an electrolyte pair in a
mixture containing many electrolyte pairs. In Eq. (5)

\[
\frac{\gamma_i, \text{H}^+}{\gamma_i, \text{NH}_4^+} = \frac{\gamma_i^2, \text{H}^+/\text{NO}_3^-}{\gamma_i^2, \text{NH}_4^+/\text{NO}_3^-} = \frac{\gamma_i^2, \text{H}^+/\text{Cl}^-}{\gamma_i^2, \text{NH}_4^+/\text{Cl}^-}.
\]  

(6)

A derivation of Eqs. (4) and (5) is given in Jacobson (1997b). Nitric acid (HNO₃) dissolution can be treated in a manner analogous to that of HCl dissolution. In Eqs. (3)--(5), \(m_{\text{H}^+}, \gamma_i, \gamma_i^+, \gamma_i^-\), and \(dC_q/dt\) must be obtained with a chemical equilibrium solver. The solver used here is EQUISOLV (Jacobson et al., 1996).

To conserve mass between the gas phase and all size bins of the particle phase, the gas-conservation equations,

\[
\frac{dC_q}{dt} = - \sum_{i=1}^{N_B} k_{q,i} \left( C_q - S_{q,i}^c C_{q,i} \right),
\]  

(7)

\[
\frac{dC_q}{dt} = - \sum_{i=1}^{N_B} k_{q,i} \left( C_q - S_{q,i}^c \frac{C_{q,i}}{H_{q,i}^c} \right)
\]  

(8)

are written for Eqs. (1) and (3), respectively, where, \(N_B\) is the number of particle size bins.

**SOLUTION TO DISSOLUTIONAL GROWTH**

Equations (3) and (8) represent \(N_B + 1\) equations that must be solved simultaneously during dissolutional growth calculations. The scheme presented here, is called the analytical predictor of dissolution (APD) scheme. It requires no iteration, conserves mass exactly, and is unconditionally stable.

The solution to the dissolutional growth equations is obtained by first assuming that the final concentration of component \(q\) in size bin \(i\) is calculated by integrating Eq. (3). The resulting expression is

\[
c_{q,i,t} = \frac{H_{q,i,t-1} C_{q,i}}{S_{q,i,t-1}}
\]

\[
+ \left( c_{q,i,t-1} - \frac{H_{q,i,t-1} C_{q,i}}{S_{q,i,t-1}} \right) \times \exp \left[ - \frac{h S_{q,i,t-1} k_{q,i,t-1}}{H_{q,i,t-1}^c} \right]
\]

(9)

where the subscripts \(t\) and \(t-1\) indicate the current time and one time step backward, respectively, and \(h\) is the time step size(s). This equation relies on a final concentration, \(C_{q,t}\), which is currently unknown. All final aerosol and gas concentrations are constrained by the mass-balance equation,

\[
C_{q,t} + \sum_{i=1}^{N_B} (c_{q,i,t}) = C_{q,t-1} + \sum_{i=1}^{N_B} (c_{q,i,t-1})
\]

(10)

Substituting Eq. (9) into Eq. (10) and solving for \(C_{q,t}\) gives

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

(11)

which is the final gas concentration. This concentration is substituted into Eq. (9) to determine final aerosol concentrations.

Observation of Eqs. (11) and (9) indicate that neither can result in a negative concentration or a concentration greater than \(C_{\text{tot}}\). Also, once Eq. (11) is derived from Eq. (10) and Eq. (10) is substituted into Eq. (9), \(C_{q,t} + \sum c_{q,i,t}\) must always equal \(C_{\text{tot}}\). Unconditional stability occurs when the absolute-value difference between a numerical and exact solution is bounded for all time, regardless of the time step (Celia and Gray, 1992). Because solutions from Eqs.
(9) and (11) are bounded between zero and \( C_{\text{tot}} \), regardless of the time step, the APD scheme is unconditionally stable. To demonstrate, assume a gas dissolves in three particle size bins, where \( k_{q,1,i-1} = 0.00333, 0.00833, \) and 0.0117 s\(^{-1}\), for the respective bins. Also, \( H_{q,i} = 4.0, S'_{q,i,i-1} = 1.0, \) and \( c_{q,i,i-1} = 0 \) \( \mu \)g m\(^{-3}\) for all bins and \( C_{q,i-1} = 10 \) \( \mu \)g m\(^{-3}\). After two hours, the APD scheme predicted \( C_{q,i} = 0.769, c_{1,q,i} = 3.08, \) \( c_{2,q,i} = 3.08, \) and \( c_{3,q,i} = 3.08 \) \( \mu \)g m\(^{-3}\), regardless of whether the time step was 0.1, 10, 60, 600, or 7200 s. In sum, the APD scheme conserves mass and is unconditionally stable.

**SOLUTION TO CONDENSATIONAL GROWTH**

Equations (1) and (7), together, represent \( N_B + 1 \) ordinary differential equations when the \( (dc_{q,i}/dt)_{eq} \) terms are split out. The method presented to solve these equations is called the *analytical predictor of condensation* (APC) scheme. The scheme does not require iteration, conserves mass exactly, and is unconditionally stable.

The APC solution is obtained by assuming that the final concentration of component \( q \) in size bin \( i \) can be integrated from Eq. (1). A resulting implicit expression is

\[
C_{q,i,t} = c_{q,i,i-1} + h k_{q,i,i-1} (C_{q,i} - S'_{q,i,i-1} C_{q,i,i-1}),
\]

where \( C_{q,i} \) is currently unknown. All final aerosol and gas concentrations are constrained by Eq. (10). Substituting Eq. (12) and Eq. (10) and solving for \( C_{q,i} \) gives

\[
C_{q,i,t} = \frac{c_{q,i,i-1} + h \sum_{n=1}^{N_B} (k_{q,i,i-1} S'_{q,i,i-1} C_{q,i,i-1})}{1 + h \sum_{n=1}^{N_B} (k_{q,i,i-1})}.
\]

The concentration from Eq. (13) cannot fall below zero but can increase above the total available mass of the species in the system. In such cases, gas concentration is limited by \( C_{q,i,t} = \min[C_{q,i,t}, C_{\text{tot}}] \). This value now serves as an estimate and is submitted into Eq. (12). Equation (12) is limited by \( c_{q,i,i} = \max[c_{q,i,i,0}, 0] \) to prevent evaporation beyond the total mass existing in each size bin. To ensure mass conservation when the latter limits are used, the final gas concentration is calculated as

\[
C_{q,i} = C_{\text{tot}} - \sum_{i=1}^{N_B} c_{q,i,i}.
\]

As with the APD scheme, the APC scheme is unconditionally stable. \( C_{q,i} \) and \( c_{q,i,i} \) are always bounded by 0 and \( C_{\text{tot}} \) and \( C_{q,i} + \sum c_{q,i,i} \) always equals \( C_{\text{tot}} \). To demonstrate, assume a gas transfers between and among three particle size bins, where \( k_{q,i,i-1} = 0.00333, 0.00833, \) and 0.0117 s\(^{-1}\), for the respective bins, \( S'_{q,i,i-1} = 1.0 \) for all three bins, \( c_{q,i,i-1} = 2, 5, \) and \( 0 \) \( \mu \)g m\(^{-3}\) for the respective bins, \( C_{q,i-1} = 3 \) \( \mu \)g m\(^{-3}\), and \( C_{q,i,i-1} = 1 \) \( \mu \)g m\(^{-3}\). After four hours, the APC scheme predicted \( C_{q,i} = 1.0, c_{q,1,i} = 2.18, c_{q,2,i} = 5.36, \) and \( c_{q,3,i} = 1.46 \) \( \mu \)g m\(^{-3}\), regardless of whether the time step was 0.1, 10, 60, 600, or 7200 s. Thus, the APC scheme conserves mass and is unconditionally stable.

**SIMULATIONS UNDER ATMOSPHERIC CONDITIONS**

Here, simulation results of condensation and dissolution coupled to equilibrium are shown for three cases representing typical conditions in coastal urban air. In all cases, the initial particle size distribution and composition contained four modes—one nucleation, two subaccumulation, and one coarse particle mode. The particles were assumed initially to contain only sulfuric acid, sodium chloride, elemental carbon, and nonreacting organic carbon. Sixteen size bins were used. The diameter of the smallest bin was 0.02 \( \mu \)m, and the volume ratio of adjacent size bins was 5.0. Figure 1 shows the initial distribution of water and ionic components in the particles when the relative humidity (r.h.) was 90% and the temperature was 298 K. The size bin struc-
APD/EQUISOLV scheme to those from the SMVGGEAR II/EQUISOLV scheme when the time interval between growth and equilibrium was 1 s in both cases. Figure 2 also shows that the growth/equilibrium solutions nearly matched a pure equilibrium solution after about two hours, indicating that gas and aerosol phases were almost in equilibrium when the relative humidity was high. Figure 3 shows a case where the time interval between growth and equilibrium calculations was increased to 15 s. A time interval of 30 s (not shown) produced smooth, but slightly less accurate results. A time interval of 60 s (not shown) produced oscillations in sulfate and bisulfate concentrations caused by delays in feedback between dissociation reactions and growth calculations.

For the second case, disolutional growth was coupled to equilibrium at r.h. = 40%. All other conditions were the same as those for the first simulation. Figure 4 shows a comparison of APD/EQUISOLV to SMVGGEAR II/EQUISOLV solutions when the time interval between growth and equilibrium calculations was 10 s. The two solutions matched almost exactly. Figure 4 also shows that growth/equilibrium results converged to pure equilibrium results. In this case, convergence took more than 10 days. In the atmosphere, perturbations, such as emissions, chemistry, and transport affect gas and aerosol concentrations over
FIGURE 4. Time-series comparison of APD/EQUISOLV results to SMVGear II/EQUISOLV results when a 10 s interval was used between growth and equilibrium. The solutions from both methods lie almost exactly on top of each other. The figure also shows equilibrium solutions (circles), calculated from EQUISOLV alone. Circle values are Na$_2$SO$_4$ = 0.583; NaCl = 0.596; NaNO$_3$ = 18.6; (NH$_4$)$_2$SO$_4$ = 0; NH$_4$Cl = 12.8; NH$_4$NO$_3$ = 19.2; and (NH$_4$)$_2$HSO$_4$ = 5.68 $\mu$g m$^{-3}$. Initial conditions were r.h. = 40%, T = 298 K, HNO$_3$(g) = 30, NH$_3$(g) = 10, and HCl(g) = 0 $\mu$g m$^{-3}$.

much shorter time periods. Thus, when the relative humidity is low, gases may not reach equilibrium with aerosols. Figure 5 shows the APD/EQUISOLV solution when the interval between growth and equilibrium calculations was 15 s. A time interval of 60 s (not shown) produced oscillations in concentrations of several species.

For the third case, cloud drop formation and with gas absorption were simulated. Growth processes accounted for included dissolution of HNO$_3$(g), NH$_3$(g), and HCl(g) and condensation of H$_2$SO$_4$(g) and H$_2$O(g). Conditions for the simulation are described in the caption for Fig. 6. The figure shows a time-series comparison of the APD/APC/EQUISOLV solution to the SMVGear II/EQUISOLV solution when the time interval between growth and equilibrium was 10 s. The solutions from the two schemes matched exactly for almost all species. Figure 7 shows the size distribution of liquid water initially, after growth, and after evaporation, for the simulations shown in Fig. 6. In the case of cloud drop growth, a longer time interval of 60 s (not shown) between growth and equilibrium calculations did not produce oscillations in concentrations because dilute solutions mollified the feedback of dissociation reactions on growth calculations.

FIGURE 5. Time-series plot of APD/EQUISOLV results when the time interval between growth and equilibrium was 15 s. Compare to Fig. 4.

COMPUTER TIMINGS

Computer timing tests were performed for the cases shown in Figs. 3 and 5. Simulation times shown are for growth and equilibrium

FIGURE 6. Time-series comparisons of APD/APC/EQUISOLV results to SMVGear II/EQUISOLV results when a 10 s interval was used between growth and equilibrium for both schemes. The two solutions lie almost exactly on top of one another for all species except liquid water. Initial conditions were T = 298 K, HNO$_3$(g) = 30, NH$_3$(g) = 10, HCl(g) = 0, and H$_2$SO$_4$(g) = 15 $\mu$g m$^{-3}$. At time zero, the r.h. 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. After forty minutes, the r.h. was reduced to 90%.
FIGURE 7. Model size distribution initially, after growth, and after evaporation obtained from the simulation shown in Fig. 6. Growth solutions for both APD/APC/EQUISOLV (APD) and SMVEAR/EQUISOLV (SMV) are shown.

calculations, together. Equilibrium calculations took more than 90% of the total time in both cases. Test were performed on the Cray J-916, a vector processing machine with a speed approximately one-fifth the speed of a Cray 90. The simulation shown in Fig. 3 required 0.179 s per grid cell per hour of simulation on the Cray J-916. For a 20,000-cell grid, this translates to about 23.9 hours per day on the Cray J-916 and 4.78 hours per day on the Cray 90. The simulation shown in Fig. 5 required 1.19 s per grid cell per hour of simulation. For a 20,000-cell grid, this translates to about 160 hours per day on the Cray J-916 and 31.9 hours per day on the Cray 90. The solution time for the low relative humidity case was greater than that for the high humidity case because more equilibrium equations were solved in the former case. The computer times of the APC and APD schemes, which are noniterative, were approximately one-half those of SMVEAR II, which is iterative. Because the matrix of partial derivatives in SMVEAR II was sparse and required no fill-in, SMVEAR II speeds were fast for this application.

CONCLUSIONS
Noniterative, unconditionally stable, mass-conserving numerical schemes were developed to solve growth equations. The analytical predictor of condensation (APC) scheme solves condensational growth equations, and the analytical predictor of dissolution (APD) scheme solves dissolution growth equations. Results from the APD and APC schemes were compared to Gear-code (SMVEAR II) results when growth was coupled to an equilibrium solver (EQUISOLV). In the three cases tested, APD/APC/EQUISOLV solutions matched SMVEAR II/EQUISOLV solutions when the time interval between growth and equilibrium was 1 s. Solutions were also good when the time interval between growth and equilibrium was 15 s. When the latter time interval is used, the coupled equilibrium/growth schemes can be used in three-dimensions. Simulation results indicated that, at a high relative humidity, growth/equilibrium approached pure equilibrium after about two hours. At a low relative humidity, equilibrium was reached after more than ten days.

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