Overhead Slides for

Chapter 13

of

Fundamentals of
Atmospheric Modeling

by

Mark Z. Jacobson

Department of
Civil & Environmental Engineering
Stanford University
Stanford, CA 94305-4020

January 30, 2002

Initial Value Problems

Vector of concentrations

$$\hat{N}_t = \left[N_{1,t}, N_{2,t}, ..., N_{i,t}, ..., N_{K,t} \right] \qquad (13.1)$$

Initial concentrations of species are known at time $t - h = 0$

$$N_{i,t-h} = N_{i,0} \qquad (13.2)$$

Properties of ODE Solvers

Accuracy

Mass conservation
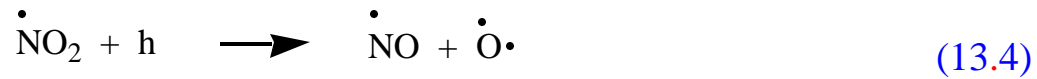
Positive-definiteness

Speed

Normalized gross error

$$\text{NGE} = \frac{1}{N_{tim}} \sum_{j=1}^{N_{tim}} \frac{1}{K_{s,t_j}} \sum_{i=1}^{K_{s,t_j}} \frac{\left| N_{i,t_j} - E_{i,t_j} \right|}{E_{i,t_j}} \times 100\% \qquad (13.3)$$

Analytical Solutions to ODEs

Example

Photolysis if nitrogen dioxide

$$\overset{\bullet}{N}O_2 + h \longrightarrow \overset{\bullet}{N}O + \overset{\bullet\bullet}{O}\bullet \qquad (13.4)$$

Time rate of change of NO_2 concentration

$$\frac{d[NO_2]}{dt} = -J[NO_2] \qquad (13.5)$$

Analytical solution

$$\boxed{[NO_2]_t = [NO_2]_{t-h}\, e^{-Jh}} \qquad (13.6)$$

$$[NO_2]_{t-h} \quad = 10^{10} \text{ molec. cm}^{-3}$$
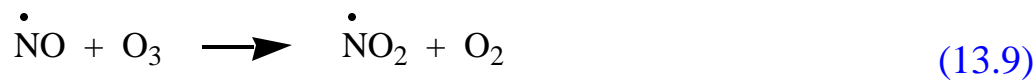
$$J \qquad = 0.02 \text{ s}^{-1}$$

$$\text{--->} \quad [NO_2]_t \qquad = 10^{10}\, e^{-0.02t}$$

Taylor Series Solution to ODEs

Explicit Taylor series expansion for one species

$$N_{i,t} = N_{i,t-h} + hN_{i,t-h} + \frac{h^2}{2}N_{i,t-h} + \frac{h^3}{6}N_{i,t-h} + ... \qquad (13.7)$$

Example

$$\dot{NO} + O_3 \longrightarrow \dot{NO}_2 + O_2 \qquad (13.9)$$

$$[NO]_t = [NO]_{t-h} + h\frac{d[NO]_{t-h}}{dt} + \frac{h^2}{2}\frac{d^2[NO]_{t-h}}{dt^2} + \frac{h^3}{6}\frac{d^3[NO]_{t-h}}{dt^3} + ...$$

$$(13.8)$$

where

$$\frac{d[NO]}{dt} = -k_b[NO][O_3] \qquad (13.10)$$

$$\frac{d^2[NO]}{dt^2} = -k_b\frac{d[NO]}{dt}[O_3] - k_b[NO]\frac{d[O_3]}{dt} \qquad (13.11)$$

$$\frac{d^3[NO]}{dt^3} = -k_b\frac{d^2[NO]}{dt^2}[O_3] - 2k_b\frac{d[NO]}{dt}\frac{d[O_3]}{dt} - k_b[NO]\frac{d^2[O_3]}{dt^2}$$

$$(13.12)$$

Taylor Series Solution to ODEs

$$\frac{d[O_3]}{dt} = -\frac{d[NO_2]}{dt} = \frac{d[NO]}{dt} \qquad\qquad (13.13)$$

$$\frac{d^2[O_3]}{dt^2} = -\frac{d^2[NO_2]}{dt^2} = \frac{d^2[NO]}{dt^2}$$

$$\frac{d^3[O_3]}{dt^3} = -\frac{d^3[NO_2]}{dt^3} = \frac{d^3[NO]}{dt^3}$$
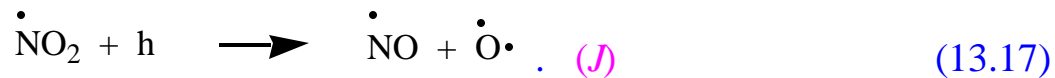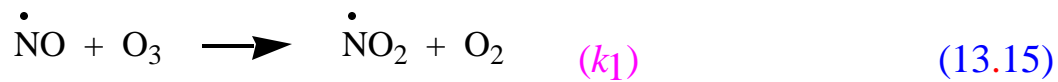
Disadvantages
        Unstable unless small time step used
        Higher derivatives cumbersome

Forward Euler Solution to ODEs

Explicit forward Euler solution for an individual species

$$N_{i,t} = N_{i,t-h} + h\dot{N}_{i,t-h} \qquad (13.14)$$

Example set of three equations

$$\dot{NO} + O_3 \longrightarrow \dot{NO}_2 + O_2 \qquad (k_1) \qquad\qquad (13.15)$$

$$\dot{NO}_2 + O_3 \longrightarrow \dot{NO}_3 + O_2, \qquad (k_2) \qquad\qquad (13.16)$$

$$\dot{NO}_2 + h \longrightarrow \dot{NO} + \dot{O}\cdot . \quad (J) \qquad\qquad (13.17)$$

First derivative of NO_2

$$\dot{N}_{NO_2,t-h} = k_1[NO]_{t-h}[O_3]_{t-h} - k_2[NO_2]_{t-h}[O_3]_{t-h} - J[NO_2]_{t-h}$$
$$(13.18)$$

Forward Euler equation

$$[NO_2]_t = [NO_2]_{t-h} + h\left(k_1[NO]_{t-h}[O_3]_{t-h} - k_2[NO_2]_{t-h}[O_3]_{t-h} - J[NO_2]_{t-h}\right)$$

$$(13.19)$$

Forward Euler Solution to ODEs

Rewrite in terms of production and loss

$$[NO_2]_t = [NO_2]_{t-h} + h\left(P_{c,NO_2, t-h} - L_{c,NO_2, t-h}\right) \qquad (13.22)$$

$$P_{c,NO_2, t-h} = k_1 [NO]_{t-h} [O_3]_{t-h} \qquad (13.20)$$

$$L_{c,NO_2, t-h} = k_2 [NO_2]_{t-h} [O_3]_{t-h} + J[NO_2]_{t-h} \qquad (13.21)$$

Advantages
  Mass conserving, easy to calculate derivatives

Disadvantage
  Unstable, requires small time step for accuracy

Backward Euler Solution to ODEs

Linearized backward Euler solution for a single species

$$N_{i,t} = N_{i,t-h} + hN_{i,t,t-h} \qquad (13.24)$$

Linearized first derivative from last example

$$N_{\mathrm{NO_2},t,t-h} = k_1[\mathrm{NO}]_{t-h}[\mathrm{O_3}]_{t-h} - k_2[\mathrm{NO_2}]_t[\mathrm{O_3}]_{t-h} - J[\mathrm{NO_2}]_t$$
$$(13.25)$$

Linearized backward Euler equation

$$[\mathrm{NO_2}]_t = [\mathrm{NO_2}]_{t-h} + h\Big(k_1[\mathrm{NO}]_{t-h}[\mathrm{O_3}]_{t-h} - k_2[\mathrm{NO_2}]_t[\mathrm{O_3}]_{t-h} - J[\mathrm{NO_2}]_t\Big)$$

$$(13.26)$$

Production term

$$P_{c,\mathrm{NO_2},t-h} = k_1[\mathrm{NO}]_{t-h}[\mathrm{O_3}]_{t-h} \qquad (13.27)$$

Loss term

$$L_{c,\mathrm{NO_2}\,t,t-h} = k_2[\mathrm{NO_2}]_t[\mathrm{O_3}]_{t-h} + J[\mathrm{NO_2}]_t \qquad (13.28)$$

Implicit loss coefficient

$$c,\mathrm{NO_2},t-h = \frac{L_{c,\mathrm{NO_2},t,t-h}}{[\mathrm{NO_2}]_t} = k_2[\mathrm{O_3}]_{t-h} + J \qquad (13.29)$$

Rewrite in terms of production and loss $\qquad (13.30)$

$$[\mathrm{NO_2}]_t = [\mathrm{NO_2}]_{t-h} + h\Big(P_{c,\mathrm{NO_2}\,t-h} - c,\mathrm{NO_2},t-h[\mathrm{NO_2}]_t\Big)$$

Backward Euler Solution to ODEs

Rearrange

$$[NO_2]_t \left(1 + h \, \eta_{c,NO_2,t-h}\right) = [NO_2]_{t-h} + hP_{c,NO_2,t-h}$$

$$\boxed{[NO_2]_t = \frac{[NO_2]_{t-h} + hP_{c,NO_2,t-h}}{1 + h \, \eta_{c,NO_2,t-h}}} \qquad (13.31)$$

Advantages

      Always gives positive solutions to chemical ODEs

Disadvantages

      Requires a small time step for accuracy
      Not mass conserving

Example of mass non-conservation

Rate of ozone loss

$$\text{Rate} = k_1 [NO]_{t-h} [O_3]_t \qquad (13.33)$$

Rate of nitric oxide loss

$$\text{Rate} = k_1 [NO]_t [O_3]_{t-h} \qquad (13.34)$$

Rate of nitrogen dioxide production

$$\text{Rate} = k_1 [NO]_{t-h} [O_3]_{t-h} \qquad (13.35)$$

Simple Exponential Solution to ODEs

Obtained by integrating a linearized first derivative.

Advantages
>   Always gives positive solutions to chemical ODEs
>   Easy to implement

Disadvantages
>   Requires a small time step for accuracy
>   Not mass conserving

Linearized first derivative from backward Euler example

$$N_{NO_2,t,t-h} = k_1[NO]_{t-h}[O_3]_{t-h} - k_2[NO_2]_t[O_3]_{t-h} - J[NO_2]_t$$

$$(13.25)$$

Rewrite in terms of production and loss

$$\frac{d[NO_2]_t}{dt} = P_{c,NO_2\,t-h} - \,_{c,NO_2,t-h}[NO_2]_t \qquad (13.36)$$

Integrate

$$[NO_2]_t = [NO_2]_{t-h}\,e^{-h\,_{c,NO_2,t-h}} + \frac{P_{c,NO_2,t-h}}{_{c,NO_2,t-h}}\left(1 - e^{-h\,_{c,\,NO_2,t-h}}\right)$$

$$(13.37)$$

Simple Exponential Solution to ODEs

Generic solution

$$N_{i,t} = N_{i,t-h}e^{-h\ \Lambda_{c,i,t-h}} + \frac{P_{c,i,t-h}}{\Lambda_{c,i,t-h}}\left(1 - e^{-h\ \Lambda_{c,i,t-h}}\right) \qquad (13.38)$$

When the implicit loss coefficient is zero (no loss term)

$$N_{i,t} = N_{i,t-h} + hP_{c,i,t-h}$$

When the production term is zero

$$N_{i,t} = N_{i,t-h}e^{-h\ \Lambda_{c,i,t-h}}$$

When implicit loss coefficient is large (short-lived species)

$$N_{i,t} = P_{c,i,t-h}/\Lambda_{c,i,t-h} \qquad \text{(steady state solution)}$$

Quasi-steady state approximation (QSSA)

$$N_{i,t} = \begin{cases} N_{i,t-h} + h\left(P_{c,i,t-h} - L_{c,i,t-h}\right) & h\Lambda_{c,i,t-h} < 0.01 \\[2ex] N_{i,t-h}e^{-h\ \Lambda_{c,i,t-h}} + \dfrac{P_{c,i,t-h}}{\Lambda_{c,i,t-h}}\left(1 - e^{-h\ \Lambda_{c,i,t-h}}\right) & 0.01 \leq h\Lambda_{c,i,t-h} \leq 10 \\[2ex] P_{c,i,t-h}/\Lambda_{c,i,t-h} & h\Lambda_{c,i,t-h} > 10 \end{cases}$$

$$(13.39)$$

Multistep Implicit-Explicit Solution

1) Set initial estimates to initial concentrations

$$N_{i,B,1} = N_{i,t-h} \tag{13.42}$$

2) Set initial maximum estimates to initial concentrations

$$N_{i,\text{MAX},1} = N_{i,t-h} \tag{13.42}$$

3) Estimate reaction rates.

$$R_{c,n,B,m} = k_n N_{i,B,m} N_{j,B,m} \tag{13.43}$$

$$R_{c,n,B,m} = J_n N_{i,B,m}$$

4) Sum production, loss, implicit loss terms

$$P_{c,i,B,m} = \sum_{l=1}^{N_{prod,i}} R_{c,n_P(l,i),B,m} \tag{13.45}$$

$$L_{c,i,B,m} = \sum_{l=1}^{N_{loss,i}} R_{c,n_L(l,i),B,m} \tag{13.47}$$

$$_{c,i,B,m} = \frac{L_{c,i,B,m}}{N_{i,B,m}} \tag{13.49}$$

Multistep Implicit-Explicit Example

Example reactions

$$\dot{\text{N}}\text{O} + \text{O}_3 \longrightarrow \dot{\text{N}}\text{O}_2 + \text{O}_2 \qquad\qquad k_1 \qquad\qquad (13.40)$$

$$\text{O}_3 + \text{h} \longrightarrow \text{O}_2 + \dot{\text{O}} \cdot \quad J$$

Estimate reaction rates.

$$R_{c,1,B,m} = k_1 [\text{NO}]_{B,m} [\text{O}_3]_{B,m} \qquad\qquad (13.44)$$

$$R_{c,2,B,m} = J [\text{O}_3]_{B,m}$$

Sum production terms

$$P_{c,\text{O},B,m} = J [\text{O}_3]_{B,m} \qquad\qquad (13.46)$$

$$P_{c,\text{NO}_2,B,m} = k_1 [\text{NO}]_{B,m} [\text{O}_3]_{B,m}$$

Sum loss terms

$$L_{c,\text{NO},B,m} = k_1 [\text{NO}]_{B,m} [\text{O}_3]_{B,m} \qquad\qquad (13.48)$$

$$L_{c,\text{O}_3,B,m} = k_1 [\text{NO}]_{B,m} [\text{O}_3]_{B,m} + J [\text{O}_3]_{B,m}$$

Sum implicit loss coefficients

$$\ell_{c,\text{NO},B,m} = k_1 [\text{O}_3]_{B,m} \qquad\qquad (13.50)$$

$$\ell_{c,\text{O}_3,B,m} = k_1 [\text{NO}]_{B,m} + J$$

Multistep Implicit-Explicit Solution

5) Estimated concentrations with backward Euler

$$N_{i,B,m+1} = \frac{N_{i,t-h} + hP_{c,i,B,m}}{1 + h \, \ell_{c,i,B,m}} \qquad (13.51)$$

6) Final concentrations with forward Euler

$$N_{i,F,m+1} = N_{i,t-h} + h\left(P_{c,i,B,m} - L_{c,i,B,m}\right) \qquad (13.52)$$

7) Check convergence
When all concentrations from forward Euler > 0 for N_P iterations in a row, convergence has occurred

$N_P = 5$ for large sets of equations
$= 30$ for small sets of equations

8) Actual final concentrations

$$N_{i,t} = \begin{cases} N_{i,B,m+1} & \left(\text{backward Euler}\right) & h \, \ell_{c,i,B,m} \geq L_T \\ N_{i,F,m+1} & \left(\text{forward Euler}\right) & h \, \ell_{c,i,B,m} < L_T \end{cases}$$

$$(13.53)$$

$L_T = 10^2 - 10^6$

9) Recalculate maximum for next iteration

$$N_{i,\text{MAX},m+1} = \max\left(N_{i,B,m+1}, N_{i,t-h}\right) \qquad (13.54)$$

$$N_{i,B,m+1} = \min\left\{N_{i,B,m+1}, N_{i,\text{MAX},m}\right\} \qquad (13.55)$$

Multistep Implicit-Explicit Solution

Iterated backward Euler solutions converge to iterated forward Euler solutions and to positive numbers.

Converged backward Euler equation

$$N_{i,B,m+1} = N_{i,t-h} + h\left(P_{c,i,B,m} - \ _{c,i,B,m} N_{i,B,m+1}\right)$$

$$(13.56)$$

Converged forward Euler equation

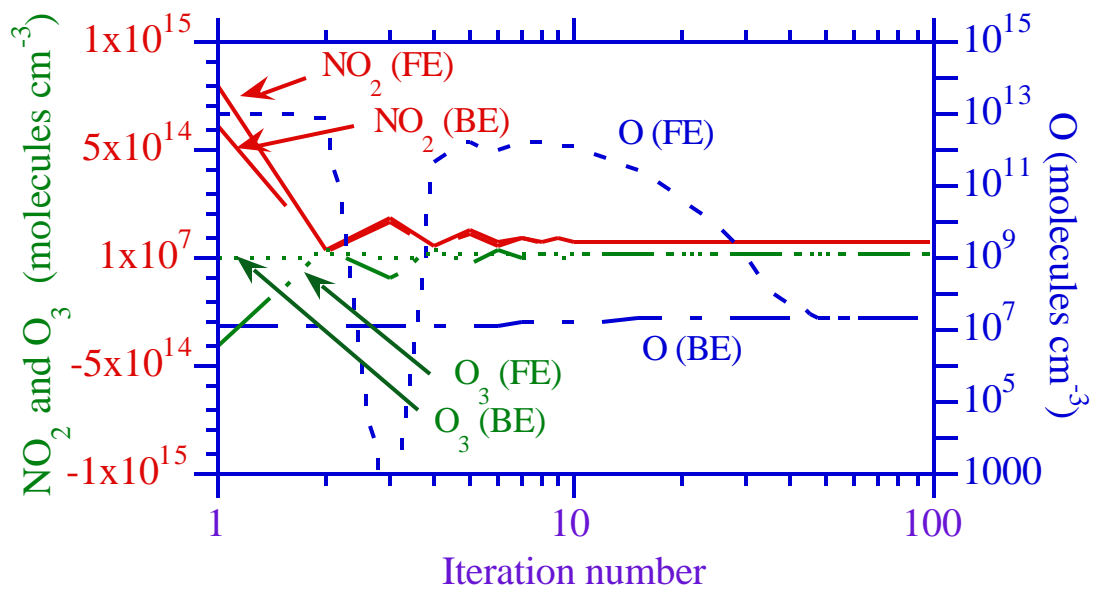$$N_{i,F,m+1} = N_{i,t-h} + h\left(P_{c,i,B,m} - \ _{c,i,B,m} N_{i,B,m}\right). \qquad (13.57)$$

where

$$_{c,i,B,m} N_{i,B,m} = L_{c,i,B,m}$$

Thus, convergence occurs when $N_{i,B,m+1} = N_{i,B,m}$

Convergence of Forward to Backward Euler

Fig. 13.1. Concentrations iterated until convergence with forward Euler (FE.) and backward Euler (BE.) calculations when $h = 10$ seconds.

# Comparison of MIE to Exact Solution

Fig. 13.2. Comparison of MIE solution (M) to an exact solution (E) for four species during a 24-hour simulation period when $h = 10$ seconds.
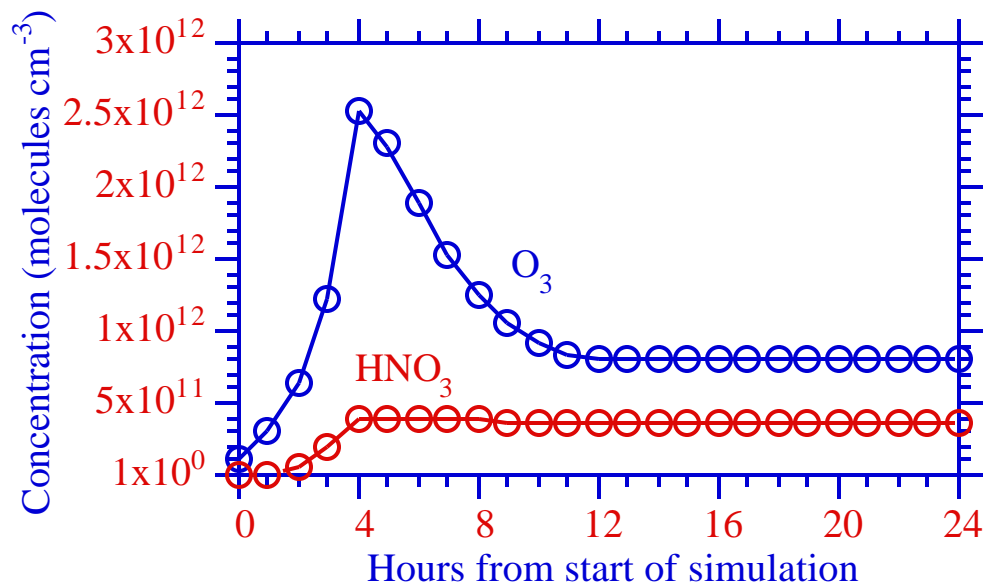
Effects of Changing the Time Step

Fig. 13.3. Effects of changing the fixed time step size with the MIE method. Time step sizes of 2, 10, 100, 500, and 1000 seconds are compared. The simulation interval is 10,000 seconds.
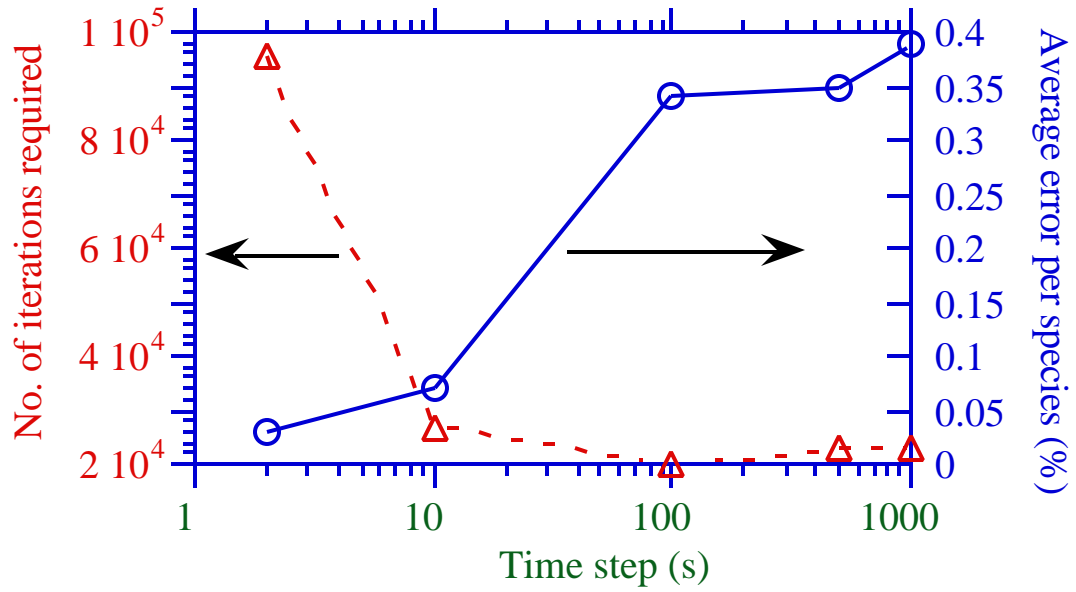
Gear's Method

Discretize time derivative in an ODE over many past steps

$$\frac{dN_{i,t}}{dt} \approx \frac{N_{i,t} - \alpha_{s,1}N_{i,t-h} - \alpha_{s,2}N_{i,t-2h}\cdots - \alpha_{s,s}N_{i,t-sh}}{h\beta_s} = \frac{N_{i,t} - \sum_{j=1}^{s}\alpha_{s,j}N_{i,t-jh}}{h\beta_s}$$

(13.59)

Rearrange for an individual species

$$0 = -N_{i,t} + \sum_{j=1}^{s}\alpha_{s,j}N_{i,t-jh} + h\beta_s \frac{dN_{i,t}}{dt}$$

(13.60)

and for a set of species

$$0 = -\hat{N}_t + \sum_{j=1}^{s}\alpha_{s,j}\hat{N}_{t-jh} + h\beta_s \frac{d\hat{N}_t}{dt}$$

(13.60)

Set up the predictor equation

$$\mathbf{P}_t\left(\hat{N}_{t,m+1} - \hat{N}_{t,m}\right) = -\hat{N}_{t,m} + \sum_{j=1}^{s}\alpha_{s,j}\hat{N}_{t-jh} + h\beta_s\hat{f}\left(\hat{N}_{t,m}\right)$$

(13.61)

Gear's Method

Simplify to

$$\mathbf{P}_t \; \hat{N}_{t,m} = \hat{B}_{t,m} \tag{13.62}$$

where

$$\hat{N}_{t,m} = \hat{N}_{t,m+1} - \hat{N}_{t,m}$$

$$\hat{B}_{t,m} = -\hat{N}_{t,m} + \sum_{j=1}^{s} {}_{s,j}\hat{N}_{t-jh} + h \; {}_{s}\hat{f}\left(\hat{N}_{t,m}\right) \tag{13.63}$$

$$\hat{f}\left(\hat{N}_{t,m}\right) = \frac{d\hat{N}_{t,m}}{dt}$$

Predictor matrix

$$\mathbf{P}_t \quad I - h \; {}_{s}J_t \tag{13.67}$$

Jacobian matrix of partial derivatives

$$J_t = J\left(\hat{N}_{t,m}\right) = \left. \frac{f_{i,t,m}}{N_{k,t,m}} \right|_{i,k=1}^{K,K} \tag{13.68}$$

Solve (13.62) for $\hat{N}_{t,m}$ and update concentration with

$$\hat{N}_{t,m+1} = \hat{N}_{t,m} + \hat{N}_{t,m} \tag{13.64}$$

Iterate until $\hat{N}_{t,m}$ 0
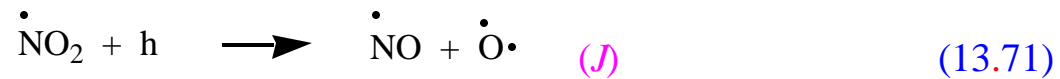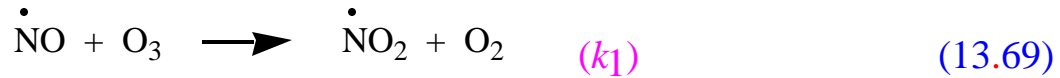
Error Tests

Local error test

$$NRMS_{t,m} = \sqrt{\frac{1}{K} \sum_{i=1}^{K} \left(\frac{N_{i,t,m}}{R_{tol} N_{i,t,1} + A_{tol,t}} \right)^2}$$
(13.65)

Global error test

$$NRMS_t = \sqrt{\frac{1}{K} \sum_{i=1}^{K} \left(\frac{\sum_m N_{i,t,m}}{R_{tol} N_{i,t,1} + A_{tol,t}} \right)^2}$$
(13.66)

Example Set of Reactions and First Derivatives

Example reactions

$$\dot{N}O + O_3 \longrightarrow \dot{N}O_2 + O_2 \qquad (k_1) \qquad (13.69)$$

$$\dot{O}\bullet + O_2 + M \longrightarrow O_3 + M \qquad (k_2) \qquad (13.70)$$

$$\dot{N}O_2 + h \longrightarrow \dot{N}O + \dot{O}\bullet \qquad (J) \qquad (13.71)$$

First derivatives of NO, NO_2, O, and O_3

$$\frac{d[NO]}{dt} = J[NO_2] - k_1[NO][O_3] \qquad (13.72)$$

$$\frac{d[NO_2]}{dt} = k_1[NO][O_3] - J[NO_2]$$

$$\frac{d[O]}{dt} = J[NO_2] - k_2[O][O_2][M]$$

$$\frac{d[O_3]}{dt} = k_2[O][O_2][M] - k_1[NO][O_3]$$

<u>Partial Derivatives</u>

Partial derivatives of NO

$$\frac{\partial^2[NO]}{\partial[NO]\,\partial t} = -k_1[O_3] \qquad\qquad \frac{\partial^2[NO]}{\partial[NO_2]\,\partial t} = J$$

$$\frac{\partial^2[NO]}{\partial[O_3]\,\partial t} = -k_1[NO] \qquad\qquad (13.73)$$

Partial derivatives of NO_2

$$\frac{\partial^2[NO_2]}{\partial[NO]\,\partial t} = k_1[O_3] \qquad\qquad \frac{\partial^2[NO_2]}{\partial[NO_2]\,\partial t} = -J$$

$$\frac{\partial^2[NO_2]}{\partial[O_3]\,\partial t} = k_1[NO] \quad (13.74)$$

Partial derivatives of O

$$\frac{\partial^2[O]}{\partial[NO_2]\,\partial t} = J \qquad\qquad \frac{\partial^2[O]}{\partial[O]\,\partial t} = -k_2[O_2][M]$$

$$(13.75)$$

Partial derivatives of O_3

$$\frac{\partial^2[O_3]}{\partial[NO]\,\partial t} = -k_1[O_3] \qquad\qquad \frac{\partial^2[O_3]}{\partial[O]\,\partial t} = k_2[O_2][M]$$

$$\frac{\partial^2[O_3]}{\partial[O_3]\,\partial t} = -k_1[NO] \qquad\qquad (13.76)$$

Predictor Matrix

	NO	NO$_2$	O	O$_3$
NO	$1 - h_s \dfrac{\partial^2 [NO]}{\partial[NO]\,\partial t}$	$-h_s \dfrac{\partial^2 [NO]}{\partial[NO_2]\,\partial t}$	$-h_s \dfrac{\partial^2 [NO]}{\partial[O]\,\partial t}$	$-h_s \dfrac{\partial^2 [NO]}{\partial[O_3]\,\partial t}$
NO$_2$	$-h_s \dfrac{\partial^2 [NO_2]}{\partial[NO]\,\partial t}$	$1 - h_s \dfrac{\partial^2 [NO_2]}{\partial[NO_2]\,\partial t}$	$-h_s \dfrac{\partial^2 [NO_2]}{\partial[O]\,\partial t}$	$-h_s \dfrac{\partial^2 [NO_2]}{\partial[O_3]\,\partial t}$
O	$-h_s \dfrac{\partial^2 [O]}{\partial[NO]\,\partial t}$	$-h_s \dfrac{\partial^2 [O]}{\partial[NO_2]\,\partial t}$	$1 - h_s \dfrac{\partial^2 [O]}{\partial[O]\,\partial t}$	$-h_s \dfrac{\partial^2 [O]}{\partial[O_3]\,\partial t}$
O$_3$	$-h_s \dfrac{\partial^2 [O_3]}{\partial[NO]\,\partial t}$	$-h_s \dfrac{\partial^2 [O_3]}{\partial[NO_2]\,\partial t}$	$-h_s \dfrac{\partial^2 [O_3]}{\partial[O]\,\partial t}$	$1 - h_s \dfrac{\partial^2 [O_3]}{\partial[O_3]\,\partial t}$

(13.77)

Predictor Matrix

	NO	NO$_2$	O	O$_3$
NO	$1 - h_s\left(-k_1[O_3]\right)$	$-h_s(J)$	0	$-h_s\left(-k_1[NO]\right)$
NO$_2$	$-h_s\left(k_1[O_3]\right)$	$1 - h_s(-J)$	0	$-h_s\left(k_1[NO]\right)$
O	0	$-h_s(J)$	$1 - h_s\left(-k_2[O_2][M]\right)$	0
O$_3$	$-h_s\left(-k_1[O_3]\right)$	0	$-h_s\left(k_2[O_2][M]\right)$	$1 - h_s\left(-k_1[NO]\right)$

(13.78)

Matrix equation $\mathbf{P}_t \; \hat{N}_{t,m} = \hat{B}_{t,m}$

$$
\begin{bmatrix}
1 - h_s\left(-k_1[O_3]\right) & -h_s(J) & 0 & -h_s\left(-k_1[NO]\right) \\
-h_s\left(k_1[O_3]\right) & 1 - h_s(-J) & 0 & -h_s\left(k_1[NO]\right) \\
0 & -h_s(J) & 1 - h_s\left(-k_2[O_2][M]\right) & 0 \\
-h_s\left(-k_1[O_3]\right) & 0 & -h_s\left(k_2[O_2][M]\right) & 1 - h_s\left(-k_1[NO]\right)
\end{bmatrix}
\begin{bmatrix}
[NO]_{t,m} \\
[NO_2]_{t,m} \\
[O]_{t,m} \\
[O_3]_{t,m}
\end{bmatrix}
=
\begin{bmatrix}
B_{NO,t,m} \\
B_{NO_2,t,m} \\
B_{O,t,m} \\
B_{O_3,t,m}
\end{bmatrix}
$$

(13.79)

Reordered Matrix

$$\begin{bmatrix} 1-h_s\left(-k_2[O_2][M]\right) & -h_s(J) & 0 & 0 \\ 0 & 1-h_s(-J) & -h_s\left(k_1[O_3]\right) & -h_s\left(k_1[NO]\right) \\ 0 & -h_s(J) & 1-h_s\left(-k_1[O_3]\right) & -h_s\left(-k_1[NO]\right) \\ -h_s\left(k_2[O_2][M]\right) & 0 & -h_s\left(-k_1[O_3]\right) & 1-h_s\left(-k_1[NO]\right) \end{bmatrix} \begin{bmatrix} [O]_{t,m} \\ [NO_2]_{t,m} \\ [NO]_{t,m} \\ [O_3]_{t,m} \end{bmatrix} = \begin{bmatrix} B_{O,t,m} \\ B_{NO_2,t,m} \\ B_{NO,t,m} \\ B_{O_3,t,m} \end{bmatrix}$$

(13.80)

Table 13.2. Effects of sparse-matrix techniques.

	Urban			Stratosphere		
	Initial	After Sparse Matrix Reductions		Initial	After Sparse Matrix Reductions	
		Day	Night		Day	Night
Order of matrix	94	94	94	43	43	43
No. init. matrix spots filled	8836	735	712	1849	292	267
% of initial positions filled	100	8.3	8.1	100	15.8	14.4
No. fin. matrix spots filled	8836	897	875	1849	337	298
% of final positions filled	100	10.2	9.9	100	18.2	16.1
No. operations decomp. 1	272,459	1978	1894	25,585	709	581
No. operations decomp. 2	4371	458	440	903	147	118
No. operations backsub. 1	4371	458	440	903	147	118
No. operations backsub. 2	4371	345	341	903	147	137

Sparse-Matrix Reductions For Large Reaction Set

1426 Species, 3905 Reactions

	Initial	After Sparse Matrix Reductions			
		Day	% Reduct-ion	Night	% Reduct-ion
Order of matrix	1426	1426		1426	
No. init. matrix spots filled	2,033,476	14,265	99.3	12,809	99.4
No. fin. matrix spots filled	2,033,476	17,090	99.2	14,925	99.3
No. operations decomp. 1	965,562,425	47,253	99.995	36,848	99.996
No. operations decomp. 2	1,016,025	9,280	99.08	7,382	99.27
No. operations backsub. 1	1,016,025	9,280	99.08	7,382	99.27
No. operations backsub. 2	1,016,025	6,384	99.37	6,117	99.40

Vectorization of Inner Nested Loop

Vectorized inner loop

Nested Loop A

```
        DO 100 NK          = 1, NBIMOLEC
          JSP1             = JPROD1(NK)
          JSP2             = JPROD2(NK)
          DO 100 K         = 1, KTLOOP
            TRATE(K,NK)    = RRATE(K,NK) *
                              CONC(K,JSP1)*CONC(K,JSP2)

 100  CONTINUE
```

Non-vectorized inner loop

Nested Loop B

```
        DO 100 K           = 1, KTLOOP
          DO 100 NK        = 1, NBIMOLEC
            JSP1           = JPROD1(NK)
            JSP2           = JPROD2(NK)
            TRATE(K,NK)    = RRATE(K, NK) *
                              CONC(K,JSP1)*CONC(K,JSP2)

 100  CONTINUE
```
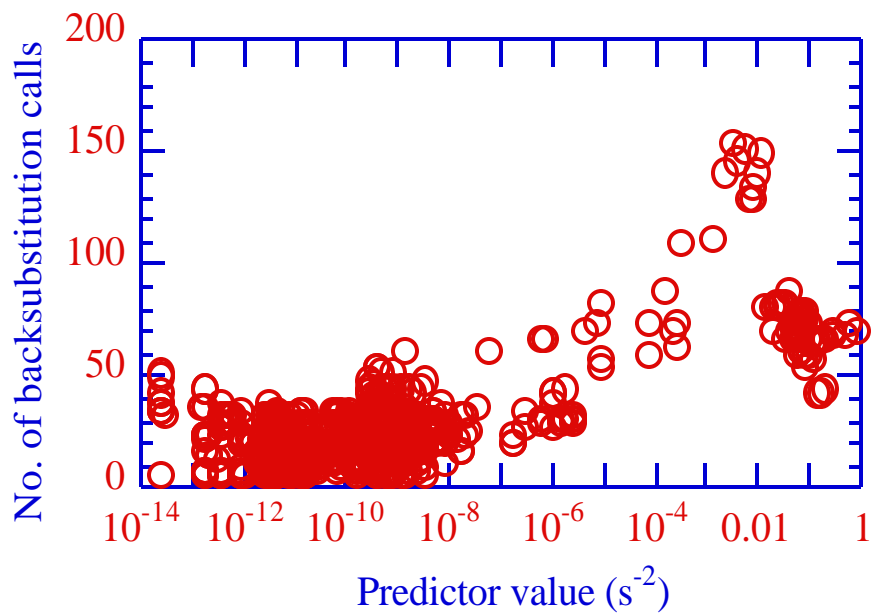
Stiffness Predictor

$$S_p = \frac{1}{K} \sum_{i=1}^{K} \left[\frac{dN_{i,t}/dt}{N_{i,t} + A_{tol,t}} \right]^2 \qquad (13.81)$$

Fig. 13.4. Number of backsubstitution during a time interval as a function of the stiffness predictor. The more backsubstitution calls, the greater the stiffness of the set of equations.
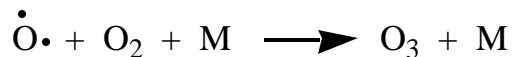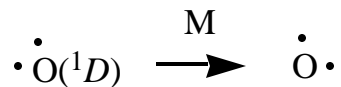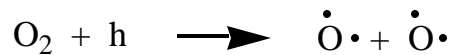
Family Method

Families

Odd Oxygen $[O_T] = [O] + [O(^1D)] + [O_3] + [NO_2]$

(13.82)

Odd Hydrogen $[HO_T] = [OH] + [HO_2] + [H_2O_2]$

(13.83)

Odd Nitrogen $[NO_T] = [NO] + [NO_2] + [NO_3]$

(13.84)

Odd Chlorine $[Cl_T] = [Cl] + [ClO] + [ClO_2]$

(13.85)

Example of species cycling within odd oxygen family

$O_3 + h \longrightarrow O_2 + \cdot \dot{O}(^1D)$

(13.86)

$O_2 + h \longrightarrow \dot{O}\cdot + \dot{O}\cdot$

$\cdot \dot{O}(^1D) \overset{M}{\longrightarrow} \dot{O}\cdot$

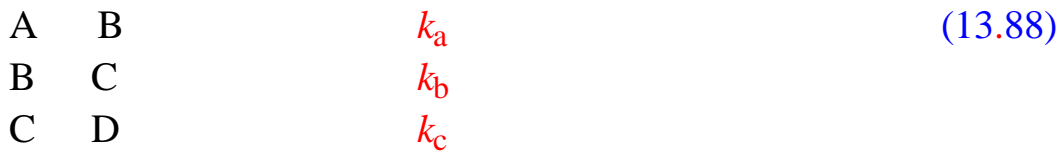$\dot{O}\cdot + O_2 + M \longrightarrow O_3 + M$

Solution With Family Method

(1) Calculate reaction rates and first derivatives

(2) Sum production and loss terms of each family

(3) Apply forward Euler to family concentration

(4) Repartition species concentrations in the family

Example with 4 total species and 2 families

$$[Fam_1] = [A] + [B] + [C] \qquad\qquad (13.87)$$

$$[Fam_2] = [D]$$

Reactions in the system

A	B	k_a	(13.88)
B	C	k_b	
C	D	k_c	

First derivatives of A, B, C, and D

$$\frac{d[A]}{dt} = -k_a[A] \qquad\qquad (13.89)$$

$$\frac{d[B]}{dt} = k_a[A] - k_b[B]$$

$$\frac{d[C]}{dt} = k_b[B] - k_c[C]$$

$$\frac{d[D]}{dt} = k_c[C]$$

Example Family Solution

First derivatives of each family as a whole

$$\frac{d[Fam_1]}{dt} = \frac{d[A]}{dt} + \frac{d[B]}{dt} + \frac{d[C]}{dt} = -k_c[C] \qquad (13.90)$$

$$\frac{d[Fam_2]}{dt} = \frac{d[D]}{dt} = k_c[C] \qquad (13.90)$$

Apply forward Euler to family concentration with

$$[Fam]_t = [Fam]_{t-h} + h\frac{d[Fam]_{t-h}}{dt} \qquad (13.91)$$

For example,

$$[Fam_1]_t = [Fam_1]_{t-h} - hk_c[C]_{t-h} \qquad (13.92)$$

$$[Fam_2]_t = [Fam_2]_{t-h} + hk_c[C]_{t-h}$$

Repartitioning Species

Repartition species concentrations in the family

Concentration of D equals second family concentration

$$[D]_t = [Fam_2]_t = hk_c[C]_{t-h}$$

Write first family conc. in terms of species concentrations

$$[Fam_1]_t = [A]_t + [B]_t + [C]_t = [A]_t \left(1 + \frac{[B]_t}{[A]_t} + \frac{[C]_t}{[A]_t} \right) \qquad (13.93)$$

Solve for A, B, and C, respectively

$$[A]_t = \frac{[Fam_1]_t}{1 + \frac{[B]_t}{[A]_t} + \frac{[C]_t}{[A]_t}} \qquad (13.94)$$

$$[B]_t = [A]_t \frac{[B]_t}{[A]_t}$$

$$[C]_t = [A]_t \frac{[C]_t}{[A]_t}$$

Many ways to obtain partitioning ratios, $\dfrac{[B]_t}{[A]_t}$ and $\dfrac{[C]_t}{[A]_t}$.

Estimating Partitioning Ratios

1) Assume each species in steady state

$$\frac{d[B]}{dt} = k_a[A] - k_b[B] = 0 \qquad\qquad (13.95)$$

$$\frac{d[C]}{dt} = k_b[B] - k_c[C] = 0$$

---> Partitioning ratios of B and C are

$$\frac{[B]_t}{[A]_t} \quad \frac{[B]}{[A]} = \frac{k_a}{k_b} \qquad\qquad (13.96)$$

$$\frac{[C]_t}{[A]_t} \quad \frac{[C]}{[A]} = \frac{[C]}{[B]}\frac{[B]}{[A]} = \frac{k_b}{k_c}\frac{k_a}{k_b} = \frac{k_a}{k_c}$$

---> Final species concentrations $\qquad\qquad$ (13.97)

$$[A]_t = \frac{[\text{Fam}_1]_t}{1 + \dfrac{k_a}{k_b} + \dfrac{k_a}{k_c}} \qquad\qquad [B]_t = \frac{[\text{Fam}_1]_t \dfrac{k_a}{k_b}}{1 + \dfrac{k_a}{k_b} + \dfrac{k_a}{k_c}}$$

$$[C]_t = \frac{[\text{Fam}_1]_t \dfrac{k_a}{k_c}}{1 + \dfrac{k_a}{k_b} + \dfrac{k_a}{k_c}}$$

Estimating Partitioning Ratios

2) First linearize the ODE of each species --

$$\frac{d[A]_t}{dt} = -k_a[A]_t \qquad\qquad (13.98)$$

$$\frac{d[B]_t}{dt} = k_a[A]_{t-h} - k_b[B]_t$$

$$\frac{d[C]_t}{dt} = k_b[B]_{t-h} - k_c[C]_t$$

-- then integrate with simple exponential method --

$$[A]_t \quad [A]_{t-h}e^{-k_a h} \qquad\qquad (13.99)$$

$$[B]_t \quad [B]_{t-h}e^{-k_b h} + \frac{k_a[A]_{t-h}}{k_b}\left(1 - e^{-k_b h}\right)$$

$$[C]_t \quad [C]_{t-h}e^{-k_c h} + \frac{k_b[B]_{t-h}}{k_c}\left(1 - e^{-k_c h}\right)$$

---> plug results into partitioning ratios

Estimating Partitioning Ratios

3) First write each species ODE in finite difference form --

$$\frac{[A]_t - [A]_{t-h}}{h} = -k_a[A]_t \qquad (13.100)$$

$$\frac{[B]_t - [B]_{t-h}}{h} = k_a[A]_t - k_b[B]_t$$

$$\frac{[C]_t - [C]_{t-h}}{h} = k_b[B]_t - k_c[C]_t$$

-- then rearrange finite difference equations into a matrix --

$$\begin{array}{ccc} 1+hk_a & 0 & 0 \\ hk_a & 1+hk_b & 0 \\ 0 & hk_b & 1+hk_c \end{array} \begin{array}{c} [A]_t \\ [B]_t \\ [C]_t \end{array} = \begin{array}{c} [A]_{t-h} \\ [B]_{t-h} \\ [C]_{t-h} \end{array} \qquad (13.101)$$

---> then solve the matrix for $[A]_t$, $[B]_t$, and $[C]_t$ and plug results into partitioning ratios

Example With Bimolecular Reaction

Add bimolecular reaction to the system

A + C   B + D k_{ac}

Linearized, finite difference forms of A, B, and C are

$$\frac{[A]_t - [A]_{t-h}}{h} = -k_a[A]_t - k_{ac}[A]_t[C]_{t-h}$$ (13.102)

$$\frac{[B]_t - [B]_{t-h}}{h} = k_a[A]_t - k_b[B]_t + 0.5k_{ac}\left([A]_t[C]_{t-h} + [A]_{t-h}[C]_t\right)$$

(13.103)

$$\frac{[C]_t - [C]_{t-h}}{h} = k_b[B]_t - k_c[C]_t - k_{ac}[A]_{t-h}[C]_t$$ (13.104)

Resulting matrix

$$
\begin{vmatrix}
1 + hk_a + hk_{ac}[C]_{t-h} & 0 & 0 \\
-hk_a - 0.5\left(hk_{ac}[C]_{t-h}\right) & 1 + hk_b & -0.5\left(hk_{ac}[A]_{t-h}\right) \\
0 & -hk_b & 1 + hk_c + hk_{ac}[A]_{t-h}
\end{vmatrix}
\begin{vmatrix} [A]_t \\ [B]_t \\ [C]_t \end{vmatrix}
=
\begin{vmatrix} [A]_{t-h} \\ [B]_{t-h} \\ [C]_{t-h} \end{vmatrix}
$$

(13.105)

---> then solve the matrix for $[A]_t$, $[B]_t$, and $[C]_t$ and plug results into partitioning ratios