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Modeling of Aqueous Chemistry in Cloud Droplets

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A Model for Aqueous Chemistry in Cloud Droplets

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Summary

The code AQCHEM.FOR, a listing of which is attached, has been prepared as a tool for the investigation of chemical reactions occurring in cloud drops. The present application is to the formation of sulfate (S(VI)) via reaction of S(IV) species with ozone and hydrogen peroxide. However, the model is constructed in a general format that allows introduction of other species and reactions easily. The model also simulates mass transfer between the liquid and gas phases, so that the assumption of equilibrium between these phases need not be invoked. Representative model simulations are presented and show good agreement with results published from similar codes. The model will be used to develop parameterizations of aqueous sulfate production rates for inclusion in a global model of the sulfur cycle.

Introduction

The impact of clouds upon trace gas species concentrations is significant. This has been shown by a number of theoretical models that have indicated that clouds significantly reduce the oxidation efficiency of the troposphere by rapidly depleting oxidants from the gas phase (Lelieveld and Crutzen, 1990; Lelieveld and Crutzen, 1991) and that clouds are a significant pathway for the conversion of sulfur dioxide, $\text{SO}_2(\text{g})$, to S(VI) species (Hegg, 1983; Hoppel et al., 1990). Variability in trace gas species due to the presence of clouds has also been demonstrated by detailed modeling studies (Thompson and Cicerone, 1982) and such variability has been observed in the field. Predictions of the uptake of gases, the conversion rates achieved, and the limiting reagents are highly sensitive to the choices made for a number of key parameters (Pandis and Seinfeld, 1989), including the droplet size, liquid water content, and gas-phase concentrations of several important species.

To study the impact of parameter choices and local conditions upon the predicted levels of sulfate produced in-cloud, a model was constructed that would allow for a variety of different initial ambient conditions to be input, and that would calculate uptake rates of gases and production of sulfate via reaction with ozone and peroxide. The sensitivity of the results to choices made for droplet sizes and accommodation coefficients can be easily studied. This document describes the model, shows how to set up the code to perform the desired type of calculation, and explains how to construct the input files needed and how to interpret the code output.

Program Modules and Function

Main (AQCHEM.FOR)

The main program calls subroutines to do the following tasks:

- read in the input file (AQINP)
- open the output files (AQOUT1, AQOUT2)
- initialize parameters (accommodation coefficients; mass-transfer coefficients; equilibrium constants)
- initialize variables (pH; effective Henry's Law constants; partition functions)
- call ODE solver (EDRIV) for required number of simulation timesteps, returning values of variables at the end of desired timesteps
- compute variables listed above at the end of each timestep
- print out information (time, variable values,...) at end of each timestep

Subroutine ACCOEFF

This subroutine is called only once. It has the values for the accommodation coefficients (aw) hardwired into it, so changes to these coefficients must be made by editing the file and changing the value of aw . Currently, a single value of aw is used for all species, but could be changed to be species-specific by dimensioning this variable. This subroutine uses the value of aw to compute $\eta(i)$, a coefficient correcting for free molecular effects in the computation of mass transfer to the droplet. η is specified by Equation (3) in Pandis and Seinfeld (1989) and is essentially the Fuchs-Sutugin correction formula. The formula requires the value of the mean free path in air and the droplet size to compute the Knudsen number, upon which the formula is based. η is currently dimensioned to the number of species to be followed, but since all accommodation coefficients have been chosen equal, all η values are equal as well.

Subroutine XKMCOEF

This subroutine computes the mass-transfer coefficients ($xmkt(i)$) using Equation (2) in Pandis and Seinfeld (1989) and is called only once. These depend inversely upon the square of the droplet radius, and directly upon η and the diffusivity of the gas-phase species ($diff$). The present implementation uses the same value of $diff$ for all species, which is read in from the input file AQINP and $diffs$ may be changed by editing that file. If it is desired to make $diff$ species-dependent, then $diff$ must be dimensioned and the subroutine which reads it modified. An alternative is to hardwire in species-dependent values of $diff$ by editing this subroutine, since only the final values of $xmkt$ will be used in the calculations.

Subroutine EQCON

This subroutine computes the gas-liquid equilibrium constants ($ek(i)$) to be used in the calculation and is called only once. THESE ARE EXTREMELY IMPORTANT, since they will be used to get effective Henry's Law constants, to compute mass transfer rates, to compute electroneutrality, and in the aqueous chemical source terms. Their numbering is crucial since there is no indication within the code as to which species each constant refers to. The current set of equilibrium constant is given in Table 1. The thermodynamic data used to compute their values is taken from Pandis and Seinfeld (1989).

Table 1a. Equilibrium Reactions (ref: Pandis and Seinfeld, 1989)

Reaction	K (298), M or M/atm	-Δ H/R, K
1 $\text{SO}_{2(g)} = \text{SO}_2 \cdot \text{H}_2\text{O}$	1.23	3120
2 $\text{SO}_2 \cdot \text{H}_2\text{O} = \text{HSO}_3^- + \text{H}^+$	1.23×10^{-2}	1960
3 $\text{HSO}_3^- = \text{SO}_3^{2-} + \text{H}^+$	6.61×10^{-8}	1500
4 $\text{H}_2\text{SO}_4(\text{aq}) = \text{HSO}_4^- + \text{H}^+$	1000	
5 $\text{HSO}_4^- = \text{SO}_4^{2-} + \text{H}^+$	1.02×10^{-2}	2720
6 $\text{H}_2\text{O}_{2(g)} = \text{H}_2\text{O}_{2(\text{aq})}$	7.45×10^4	6620
7 $\text{HNO}_{3(g)} = \text{HNO}_{3(\text{aq})}$	2.1×10^5	
8 $\text{HNO}_{3(\text{aq})} = \text{NO}_3^- + \text{H}^+$	15.4	8700
9 $\text{O}_{3(g)} = \text{O}_{3(\text{aq})}$	1.13×10^{-2}	2300
10 $\text{NH}_{3(g)} = \text{NH}_4\text{OH}(\text{aq})$	75	3400
11 $\text{NH}_4\text{OH}(\text{aq}) = \text{NH}_4^+ + \text{OH}^-$	1.75×10^{-5}	-450
12 $\text{H}_2\text{O} = \text{H}^+ + \text{OH}^-$	1.0×10^{-14}	-6710

Table 1b. Sulfate Formation Rate Expressions Used (Seinfeld, 1986)

TABLE 5.11. Rate Expressions for Sulfate Formation in Aqueous Solution Used in Computing Figure 5.8

Oxidant	Rate Expression, $-\frac{d[\text{S(IV)}]}{dt}$	
O_3	$(k_0[\text{SO}_2 \cdot \text{H}_2\text{O}] + k_1[\text{HSO}_3^-] + k_2[\text{SO}_3^{2-}])[\text{O}_3(\text{aq})]$ $k_0 = 2.4 \times 10^4 \text{ M}^{-1} \text{ sec}^{-1}$ at 298 K $k_1 = 3.7 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$ $k_2 = 1.5 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$	Hoffmann and Calvert (1985)
H_2O_2	$\frac{k[\text{H}^+][\text{HSO}_3^-][\text{H}_2\text{O}_2(\text{aq})]}{1 + K[\text{H}^+]}$ $k = 7.45 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$ at 298 K $k = 13 \text{ M}^{-1}$	Hoffmann and Calvert (1985)

To ADD equilibria, do so at the END of the present list of reactions, so that the numbering of the original $ek(i)$ need not be disturbed. Also remember to redefine $neql$, set in DROPCL, which tells the code the dimension of $ek(i)$.

Subroutine PARTFCN

This subroutine computes the partition function for each gas-phase species ($pf(i)$) and is called at time zero and at the completion of each timestep. The partition function is defined as in Chameides (1984), Equation (12):

$$PF(I) = [I] / ([I(g)] Heff(I) RT)$$

where $[I]$ indicates the aqueous-phase concentration of species I, and $[I(g)]$ indicates the gas-phase concentration of that species, $Heff(I)$ is the effective Henry's Law constant, R is the gas constant, and T is the temperature in Kelvin. When $PF(I) = 1$, the species is in equilibrium; if $PF < 1$, the species is undersaturated in the aqueous phase; if $PF > 1$, the species is supersaturated in the aqueous phase. By following the time-dependent variation of $pf(i)$, it can be seen which species respond quickly to changes in external conditions and which species do not achieve gas-liquid equilibrium on timescales similar to those of the cloud.

Subroutine RDINPUT

This subroutine reads the file AQINP, assigns values to parameters and variables, and processes any comment text for output. It uses functions that may be specific to the machine the code was written for. Please consult John Hobson of G-Division if problems arise with this subroutine.

Subroutine DIFFUN

This subroutine is required by the ODE solver and supplies the solver with values of derivatives. (Note: DO NOT change the arguments in the call, since they are defined by the solver.) The subroutine is passed current species concentrations (ya) which are used to compute the derivatives. The derivatives are based upon the conservation equations given in Pandis and Seinfeld (1989), Equations (1) and (5), but have been modified to allow for gas-phase sources.

The gas-phase conservation equations contain the difference between the aqueous and gas-phase concentrations of the species (the factor $(Heff RT)^{-1}$ converts to the correct units), multiplied by the mass transfer coefficient ($xkmt$) and the liquid water content (wl). Note that when the difference goes to zero, the equilibrium expression is recovered, consistent with a zero driving force for transfer to either phase. The derivative also includes the term $rsrc(i)$, which is simply the total gas-phase source of that species. The value of all the $rsrc(i)$ are computed in the subroutine RSOURCE, called prior to the derivative calculation. Since RSOURCE and Heff require current pH values, the electroneutrality subroutine ELECNEUT called first.

The aqueous-phase conservation equations are similar to those for the gas, but the sign of the difference is reversed, and the factor wl is not needed. For the aqueous phase, the $rsrc(i)$ are the production rates of aqueous species in the solution.

The species S(VI) is assumed to partition completely into the aqueous phase, so that its conservation equation does not contain the term representing interfacial mass transfer.

Subroutine HENRY

This subroutine is called repeatedly during the simulation. It computes current values of the effective Henry's Law constants, which depend upon the pH. Five $heff(i)$ are computed, representing the 5 gas-phase species followed in the calculation. If more species are to be included, the dimension of $heff(i)$ must be changed, and the expressions included in this subroutine. The new $heff(i)$ will also require additional equilibrium constants that should be put into EQCON, as discussed above.

Subroutine RSOURCE

This subroutine is called from DIFFUN to get species production rates. Current values of species concentrations (ya), time (t) and pH (h) are passed to it, so the source rates may be written as dependent upon these variables.

Several options for source rates are possible:

- zero sources in gas phase ("closed" system)
- source of gas phase species selected to just balance consumption by reaction in the aqueous phase ("open" system)
- source of gas phase species specified externally as function of some variables, for example, using derivatives computed from gas-phase only chemistry simulation

Further comments concerning these choices are made in the program itself and in the discussion of types of ambient conditions to be simulated.

In the version of the code supplied with this document, expressions for the formation of S(VI) due to oxidation of S(IV) species by O_3 and H_2O_2 are included. The rate expressions used are given in Table 1b and are taken from Table 5.11 in Seinfeld (1986).

Subroutine ELECNEUT

This subroutine computes the pH of the solution, given current values for the constituent ions, using the charge neutrality requirement. To keep this subroutine as non-specific as possible, it simply calls other subroutines to get the total quantity of positive charges and the total quantity of negative charges, and then uses a Newton's method to focus in on the appropriate pH. For the Newton's method, derivatives with respect to pH must be computed; these are also done in separate routines for the positively and negatively charged ions to be considered. This scheme makes it simple to add or subtract ionic species, by going into the subroutines POS, CNEG, DPOS, and DNEG, without modifying the electroneutrality scheme.

Probably the only change that may be desired in this subroutine is the stringency of the convergence check. Currently, the normalized function to be zeroed must be <0.00001 . The alternative check, used if repeated updates on pH affect the value of pH very little, is that the normalized difference between successive guesses at $[H^+]$ must be >0.0001 .

A special version of ELECNEUT may be used if a simulation is desired in which the pH is held constant at an arbitrary value. To accomplish this, the coding in ELECNEUT must be replaced with a single line stating " $h=(\text{desired value})$ ". An example is given later in this report (see Example 7).

Subroutines POS and CNEG

The subroutines compute the concentrations of positive and negative ions in solution. Since the variables used in the integration often represent a related set of aqueous species (total [S(IV)], for example), aqueous equilibrium reactions must be used to break the "family" variable into its ionic constituents. All expressions should contain only values of $ya(i)$ and h , besides the equilibrium constants. This facilitates taking derivatives with respect to $[H^+]$. The derivation of the expressions used in POS and CNEG are given in Appendix A.

Subroutines DPOS and DNEG

These subroutines simply compute the derivative of total positive ion and total negative ion concentrations with respect to $[H^+]$. The derivation of the expressions used in DPOS and DNEG are given in Appendix A.

Other Files Needed

DROPCL

This is a cliche file which is used by the MAIN and most of the subroutines through the 'include dropcl' statement. Parameter values for *neqn* (number of differential equations), *nspec* (number of species) and *neql* (number of equilibrium reactions) are set here, as well as the dimensions of a number of variables. It also contains common blocks needed in the subroutines.

AQINP

This is the input file for the code. Comments concerning the specific simulation may be included by beginning a line with " ". All comments appear in the file "AQOUT1". The example file also shows the species numbering used in the code. IF THIS NUMBERING IS CHANGED, A SIGNIFICANT NUMBER OF STATEMENTS IN THE CODE MUST BE MODIFIED. It is not recommended that the numbering be changed. If a species is not desired, its initial value may be set to zero and all production and loss rates set to zero. Alternatively, set its initial value to zero and set its derivative to zero in DIFFUN.

Values must be given for the following variables:

y 1 through y 11	initial species concentrations. UNITS: gas phase, moles/L gas; aqueous phase, mol/L water.
temp	temperature, deg Kelvin
wl	liquid water content, L water/ L air
rad	droplet radius, cm
xmfp	mean free path, cm
diff	gas diffusivity, cm ² /s
gasc	gas constant, 0.082058 L atm/mol K
xo	initial time, sec
ho	initial internal timestep, sec
xstep	timesteps at which output desired, sec
iters	number of timesteps to take
mf	method flag for solver; "22" is for stiff systems, internally-approximated Jacobian

EPISLIB

This is the library which contains the ODE solver. It must reside on the disk when a new version of the executable program is being created.

LODAQ (Optional)

This contains the command to create the executable file, XAQCHEM.

Commands to compile and execute

The code was compiled using CFT77 on the NERSC C machine. Type "cft77 -ezs aqchem.for".

To create the executable, XAQCHEM, type "ldr df=lodaq".

Alternatively, type "ldr bin=aqchem.for.o, lib=(fortlib,epislib), x=xaqchem"

To run, type "xaqchem".

Note: Be sure you have the desired AQINP file on disk first. Also check that there are no files called AQOUT1 or AQOUT2 on disk, since these are called "new" files when opened in the code. This will prevent overwriting of previously-generated data files. The best practice is to rename the two output files after each run is completed.

Output Files

AQOUT1

This output file contains the following:

First entry (variable number of lines): Repeats the AQINP file used in the simulation.

Next line: values of $\eta(i)$, the Fuchs-Sutugin correction factor, $i=1, n_{\text{spec}}$

Next line: Values of $x_{\text{mt}}(i)$, the mass transfer coefficients, $i=1, n_{\text{spec}}$

Next line: Values of $ek(i)$, the equilibrium constants, $i=1, n_{\text{eq}}$

All subsequent lines: output of time-dependent calculation in the format:

time (sec) $y_a(i)$, $i=1,11$; units as described in AQINP pH

AQOUT2

This output file contains the following:

All lines: output of time-dependent calculation in the format:

time (sec) pH effective Henry's Law constants, $heff(i)$, $i=1,5$ Partition functions, $pf(i)$, $i=1,5$

Note: Rename these two files to save them after a run, or delete them from the disk (see Note under "Commands to compile and execute" above).

Listing of Code Developed:

AQCHEM.FOR

with files

DROPCL, LODAQ, AQINP (Example)

```

c
c program AQCHEM.FOR:
c                               Sonia Kreidenweis and John Hobson, October 1991
c
c  References:
c    Pandis and Seinfeld, JGR 94(D1), 1105-1126, 1989.
c    Chameides, JGR 89(D3), 4739-4755, 1984.
c    Lelieveld and Crutzen, J. Atm. Chem. 12, 229-267, 1991.
c
c    Computes both rate of transfer of species between aqueous
c    and gas phases, and rate of reaction in aqueous
c    Gas-phase sources may be specified by user
c
c    include 'dropcl'
c
c First read text from input file that gives nature of problem, and
c specifies species and their numbering.
c Next, read initial values for all species.
c
c  UNITS: gas-phase species are to be given in mol/L gas
c    aqueous-phase species are to be given in mol/L water
c    unit conventions follow Pandis and Seinfeld
c
c Read in external conditions: temperature in K, liquid water content
c (L water/L air), droplet radius (cm), mean free path (cm),
c diffusivity (cm2/s), gas constant (L atm/mol K).
c
c Read in information for ODE solver, including number of ODEs to solve (NEQNS)
c    call dropfile(0)
c    nt = 5
c    call ioscale
c    call msglink(nt,1)
c    open(20,file='aqout1',status='new')
c    open(21,file='aqout2',status='new')
c    call rdinput(ya)
c
c Set error tolerance to 1.e-5, and error control method to ierror=3
c
c    tol=1.e-5
c    ierror=3
c
c Call subroutine that contains accommodation coefficients to be used
c (user supplies this subroutine)
c
c    call accoeff
c    write(20,'(1x,"etas",11e10.3)') (eta(i),i=1,neqn)
c
c Call subroutine that computes the mass-transfer coefficients
c
c    call xkmcoef
c    write(20,'(1x,"kmt",11e10.3)') (xkmt(i),i=1,neqn)
c
c Call subroutine to calculate the equilibrium constants, ek(nspec)
c
c    call eqcon
c    write(20,'(1x,"ek",13e10.3)') (ek(i),i=1,neq1)
c
c Compute the initial drop pH. Use pH=7 as initial guess
c
c    h=1.e-7
c    call elecneut(ya,h)
c    call henry(h)
c    call partfcn(ya)
c
c Print out all initial information: copy all input files to

```

[illegible]

[illegible]


```

        elseif(iout(1) .eq. 'diff') then
            diff = xout(2)
        elseif(iout(1) .eq. 'gasc') then
            gasc = xout(2)
        elseif(iout(1) .eq. 'xo') then
            xo = xout(2)
        elseif(iout(1) .eq. 'ho') then
            ho = xout(2)
        elseif(iout(1) .eq. 'xstep') then
            xstep = xout(2)
        elseif(iout(1) .eq. 'iters') then
            iters = inout(2)
        elseif(iout(1) .eq. 'mf') then
            mf = inout(2)
        elseif(iout(1) .eq. '**') then
        else
            msg = 'input ignored: '//iout(1)//' ...'
            write(*,*) msg
            write(20,*) msg
        endif
        go to 100
1000 continue
        hmax = .1*xstep
        close(10)
        return
    end

C
c SSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSS
c
        subroutine diffun(neqns,t,ya,yderiv)
            include 'dropcl'
            dimension rsrc(nspec)

C
c Compute the current pH using the values of the aqueous-phase species
c
            call elecneut(ya,h)

C
c Use pH to compute the current values of the modified Henry's Law coeff
c
            call henry(h)

C
c Compute current values of chemical source rates
c
            call rsource(ya,rsrc,h,t)

C
c Species conservation equations: gas-phase
c
c -----*-----
c Note that 5 gas-phase species are hard-wired in here. If this is to be c changed,
remember to carry changes into this subroutine
c Same idea for aqueous-phase species and S(VI)
c -----
c
            rt=gasc*temp
            do 10 i=1,5

C
c following is normal conservation equation:
c
                yderiv(i)=xkmt(i)*w1*((ya(i+5)/(heff(i)*rt))-ya(i))+rsrc(i)

C
c following is to keep gas phase concentrations constant (open system)
c
                yderiv(i)=0.
c

```

```

10      continue
c
c Species conservation equations: aqueous-phase
c
      do 20 i=6,10
        yderiv(i)=xkmt(i)*(ya(i-5)-(ya(i)/(heff(i-5)*rt)))+rsrc(i)
20    continue
c
c species without gas-liquid equilibrium: S(VI)
c
      yderiv(11)=rsrc(11)
c
      return
end
c
c =====
c subroutine henry(h)
c Needs 12 equilibrium constants to do calculation; these are ek(i)
c
c include 'dropcl'
c h is the concentration of [H+]. heff is the effective Henry's Law constant
c -----
c Right now 5 Henry's Law coefficients are hardwired in. Input more
c equaitons into this subroutine and change dimension in "dropcl"
c -----
c
      heff(1)=ek(1)*(1+(ek(2)/h)+(ek(2)*ek(3)/(h**2)))
      heff(2)=ek(9)
      heff(3)=ek(6)
      heff(4)=ek(10)*(1+(ek(11)*h/ek(12)))
      heff(5)=ek(7)*(1+(ek(8)/h))
c
      return
end
c
c =====
c subroutine rsource(ya,rsrc,h,t)
c Needs to have rate constants passed to it; also, for
c computing reaction rates, needs current conc's of reactants
c
c dimension rsrc(11)
c include 'dropcl'
c .
c -----
c User supplies this subroutine according to reaction rates desired
c Change dimension of rsrc(i) if this is modified
c -----
c
c Compute the source rates of each species for which conservation eqn written
c Can be constant sources, zero sources (closed system), or chemical reaction
c
c Species numbering:
c   1 SO2(g)           6 S(IV)(aq)
c   2 O3(g)            7 O3(aq)
c   3 H2O2(g)          8 H2O2(aq)
c   4 NH3(g)           9 N(III)(aq)
c   5 HNO3(g)         10 N(V)(aq)
c                   11 S(VI)(aq)
c
c source of S(VI) is reactions 1 and 2 in aqueous phase, due to O3 and H2O2
```

[illegible]

[illegible]

```
C      cnh4=ya(9)/(1.+ek(12)/(ek(11)*h))  
C  
C      posions=h+cnh4  
C      return  
C      end  
  
C  
C SSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSS  
C  
C      subroutine cneg(ya,h,cnregions)  
C      include 'dropcl'  
  
C Subroutine computes the concentrations of negative ions  
C -----  
C User supplies this subroutine according to neg-charged species used  
C -----  
C Note that some are reexpressed in terms of known quantities - see  
C writeup for derivations  
C Needs equilibrium constants - passss via dropcl  
C In this problem, negative ions are OH-, HSO3-, SO3=, SO4=, HSO4-, NO3-  
C  
C      oh=ek(12)/h  
C      cno3=ya(10)/(1.+(h/ek(8)))  
C      hso4=ya(11)/(1.+(ek(5)/h)-(h/ek(4)))  
C      so4=ek(5)*hso4/h  
C      hso3=ya(6)/(1.+(h/ek(2))+((ek(3))/h))  
C      so3=ek(3)*hso3/h  
  
C      cnegions=oh+hso3+(2.*so3)+(2.*so4)-hso4+cnc3  
C      return  
C      end  
  
C SSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSS  
C  
C      subroutine dpos(ya,h,dposi)  
C      include 'dropcl'  
  
C Subroutine computes the deriv. of concentrations of positive ions  
C -----  
C Change according to structure of "pos"  
C -----  
C Note that some are reexpressed in terms of known quantities - see  
C writeup for derivations  
C Needs equilibrium constants - passss via dropcl  
C In this problem, positive ions are H+,and NH4+. NH4+ is in terms of N III  
C  
C      dnh4=(ya(9)/(((1.+ek(12)/(ek(11)*h))*2))*(ek(12)/(ek(11)*(h**2))))  
  
C      dposi=1.+dnh4  
C      return  
C      end  
  
C SSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSS  
C  
C      subroutine dnega(ya,h,dnega)  
C      include 'dropcl'
```

[illegible]

```

c 'dropcl': contains common blocks and parameter and dimension
c statements to be used in program
c
      parameter (neqn=11)
      parameter (nspec=11)
      parameter (neql=12)
c
      dimension ya(neqn),yderiv(neqn)
      dimension eta(nspec), xkmt(nspec), pf(5)
      dimension ek(neql), heff(5)
c
      common /inp/temp,wl,rad,xmfp,diff,gasc,eta,xkmt
      common /eq/ek,heff,pf,hconc
      dimension ymax(neqn)
      common /ode/ xo,ho,tol,mf,index,ymax,hmax,xstep,itors,ierror

```

Following is "lodaq":

```
bin=aqchem.for.o,lib=(fortlib,epislib),x=xaqchem
```

EXAMPLE AQINP FILE

```
* EXAMPLE 1:
* Approach to equilibrium
* Description of problem:
* Beginning with initial gas-phase concentrations of SO2, H2O2, NH3,
* HNO3, and O3, compute the uptake by droplets
* Species included and ordering:
* 1  SO2 g
* 2  O3 g
* 3  H2O2 g
* 4  NH3 g
* 5  HNO3 g
* 6  S(IV) = SO2 aq + HSO3- + SO3=
* 7  O3 aq
* 8  H2O2 aq
* 9  N(III) = NH4OH + NH4+
* 10 N(V) = HNO3 aq + NO3-
* 11 S(VI) = H2SO4 aq + HSO4- + SO4=
*
y 1 2.045e-10
y 2 2.045e-10
y 3 4.09e-11
y 4 2.045e-10
y 5 4.09e-11
y 6 0.
y 7 0.
y 8 0.
y 9 0.
y 10 0.
y 11 0.
temp 298.
wl 1.e-6
rad 10.e-4
xmfp .065e-4
diff 0.1
gasc 0.082058
xo 0.
ho .001
xstep 0.1
iters 10
mf 22
```

INSERT
COMMENTS WITH *

KEEP ORDER OF
SPECIES HERE FOR
REFERENCE

INITIAL VALUES OF
SPECIES CONC

THESE PARAMETERS
MUST BE SET HERE

SEE DOCUMENT FOR
DEFINITIONS

Simulation Scenarios with Examples

1. Approach to Equilibrium

The simplest implementation of the code is to calculate the equilibrium distribution of given total species concentrations. This may be done in a time-dependent mode, to investigate the effects of mass transfer limitations and solubility (effective Henry's Law constant) upon the time required to reach equilibrium. The code output will also show the equilibrium solution pH.

- (a) AQINP file: List initial values for species desired. Specify timestep to be investigated. Set temperature, liquid water content, etc.
- (b) AQCHEM.FOR: Set $r_{src}(i)=0$.
- (c) Compile and link.

Example: Compare the approach to equilibrium of SO_2 , HNO_3 , H_2O_2 , and NH_3 .

See AQINP file, DIFFUN and RSOURCE used (Fig. EX1A), output files (Fig. EX1B), and plot (Fig. EX1C).

Compare with Figure 2 of Chameides (1984) (shown as Fig. EX1D). Highly soluble species (HNO_3) may not reach thermodynamic equilibrium during cloud lifetime because so much mass must be transferred from the gas phase.

The conversion from the standard units to ppb is shown in Table EX1. These may be compared with the equilibrium conditions given in the example in Seinfeld (1986). It is seen that they are quite similar.

2. Production of Sulfate in "Closed" System Initially at Thermodynamic Equilibrium

The initial condition chosen for a study of aqueous reaction rates may be that the system is initially in equilibrium with the gas phase. A "closed" system means that there are no gas-phase sources, so that the total amount of $\text{SO}_2 + \text{S(IV)} + \text{S(VI)}$, for example, remains constant.

- (a) Run a Type 1 simulation (above) to find equilibrium gas and aqueous concentrations to use as initial conditions.
- (b) AQINP file: Initialize with equilibrium concentrations and set appropriate timesteps.
- (c) AQCHEM.FOR: Set $r_{src}(i)$ to compute depletion of S(IV) , O_3 , and H_2O_2 and to compute production of S(VI) .
- (d) Compile and link.

Example: Reproduce example on pages 239-241 of Seinfeld (1986) (reproduced on next page).

See AQINP file and RSOURCE used (Fig. EX2A), output files (Fig. EX2B), and plot (Fig. EX2C). Compare with Figures 5.15 and 5.16 of Seinfeld (1986); the behavior is similar. Sulfate production is limited in the closed system due to depletion of the oxidants.

From Seinfeld (1986).

The concentrations of each ion except $[\text{SO}_4^{2-}]$ can be expressed in terms of $[\text{H}^+]$ using the equilibrium constant expressions,

$$[\text{NH}_4^+] = \frac{K_{a,w} K_{a1}}{K_w} p_{\text{NH}_3} [\text{H}^+]$$

$$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]}$$

$$[\text{HSO}_3^-] = \frac{K_{a2} K_{a1}}{[\text{H}^+]} p_{\text{SO}_2}$$

$$[\text{SO}_3^{2-}] = \frac{K_{a2} K_{a1} K_{a2}}{[\text{H}^+]^2} p_{\text{SO}_2}$$

$$[\text{NO}_3^-] = \frac{K_{a3} K_{a3} p_{\text{HNO}_3}}{[\text{H}^+]}$$

If we define $[\text{S(VI)}] = [\text{SO}_4^{2-}] + [\text{HSO}_4^-] + [\text{H}_2\text{SO}_4(\text{aq})]$, then

$$[\text{HSO}_4^-] = \frac{[\text{S(VI)}]}{\frac{[\text{H}^+]}{K_{a3}} + 1 + \frac{K_{a4}}{[\text{H}^+]}}$$

$$[\text{SO}_4^{2-}] = \frac{[\text{S(VI)}]}{\frac{[\text{H}^+]^2}{K_{a3} K_{a4}} + \frac{[\text{H}^+]}{K_{a4}} + 1}$$

where K_{a3} and K_{a4} are the equilibrium constants for the reaction,

respectively. For all practical purposes K_{a3} may be considered to be infinite since virtually no undissociated sulfuric acid will exist in solution, and $K_{a4} = 1.2 \times 10^{-2} \text{ M}$ at 298 K.

The concentration changes are computed as follows. At $t = 0$, if no S(VI) is present, the electroneutrality equation is solved to determine $[\text{H}^+]$ and, thereby, the concentrations of all the dissolved species. If an open system is assumed, then the gas phase partial pressures will remain constant with time. If a closed system, the partial pressures change with time as outlined above.

concentration changes are computed over small time increments of length Δt . The sulfate present at any time t is equal to that at time $t - \Delta t$ plus that formed in the interval Δt ,

$$[\text{SO}_4^{2-}]_t = [\text{SO}_4^{2-}]_{t-\Delta t} + \left(\frac{d[\text{SO}_4^{2-}]}{dt} \right)_{t-\Delta t} \Delta t$$

The value of $[\text{SO}_4^{2-}]$ at time t is then substituted into the electroneutrality equation to obtain the new $[\text{H}^+]$ and the concentrations of other dissolved species. This process is then just repeated over the time interval of interest.

Let us compare the evolution of open and closed systems for an identical set of starting conditions. We choose the following conditions at $t = 0$:

$$\begin{aligned} [\text{S(IV)}]_{\text{total}} &= 5 \text{ ppb} & \text{pH} &= 6.17 \\ [\text{HNO}_3]_{\text{total}} &= 1 \text{ ppb} & L &= 10^{-6} \\ [\text{NH}_3]_{\text{total}} &= 5 \text{ ppb} \\ [\text{O}_3]_{\text{total}} &= 5 \text{ ppb} \\ [\text{H}_2\text{O}_2]_{\text{total}} &= 1 \text{ ppb} \end{aligned}$$

For the closed system, there is no replenishment, whereas in the open system the partial pressures of all species in the gas phase are maintained constant at their initial values and aqueous-phase concentrations are determined by equilibrium. The initial gas-phase concentrations in both cases are:

$$\begin{aligned} p_{\text{SO}_2} &= 3.03 \text{ ppb} & p_{\text{O}_3} &= 5 \text{ ppb} \\ p_{\text{NH}_3} &= 1.87 \text{ ppb} & p_{\text{H}_2\text{O}_2} &= 0.465 \text{ ppb} \\ p_{\text{HNO}_3} &= 8.54 \times 10^{-9} \text{ ppb} \end{aligned}$$

In the open system these partial pressures remain constant throughout the simulation, whereas in the closed system they may be depleted. A comment concerning the choice of O_3 concentration is in order. We selected the uncharacteristically low value of 5 ppb so as to be able to show the interplay possible between both the H_2O_2 and O_3 oxidation rates and, in the closed system, the role of depletion as the reaction proceeds. However, even at O_3 of 50 ppb the dynamics of the system are dominated by the great reduction in O_3 oxidation of S(IV) as pH drops and by the depletion of H_2O_2 in the closed system.

Figures 5.15 and 5.16 show the sulfate concentration and pH , respectively, in the open and closed systems over a 60-minute period.

More sulfate is produced in the open system than in the closed system, but the pH decrease is less in the open system. This behavior is a result of several

Figure 5.15. Aqueous sulfate concentration as a function of time for both open and closed systems. The conditions for the simulation are: $[S(IV)]_{\text{total}} = 5 \text{ ppb}$; $[NH_3]_{\text{total}} = 5 \text{ ppb}$; $[HNO_3]_{\text{total}} = 1 \text{ ppb}$; $[O_3]_{\text{total}} = 5 \text{ ppb}$; $[H_2O_2]_{\text{total}} = 1 \text{ ppb}$; $I = 10^{-6}$; $pH_0 = 6.17$.

factors:

1. Sulfate production due to H_2O_2 and O_3 is less in the closed system due to depletion of H_2O_2 and O_3 .
2. Continued replenishment of NH_3 provides more neutralization in the open system.
3. The low pH in the closed system drives $S(IV)$ from solution.
4. The lower pH in the closed system depresses the rate of sulfate formation by O_3 .
5. $S(IV)$ is continually depleted in the closed system.
6. Total HNO_3 decreases in the open system due to the decrease in pH.

In the open system the importance of H_2O_2 in sulfate formation grows significantly, from less than 20 percent to over 80 percent, whereas in the closed system the increasing importance of H_2O_2 is enhanced at lower pH but suppressed by the depletion of H_2O_2 . The depletion effect predominates so that after about 30 min sulfate formation ceases in the closed system. The fractions of SO_2 , O_3 , and H_2O_2 reacted in the closed system at 60 min are

Figure 5.16. pH as a function of time for both open and closed systems. Same conditions as Figure 5.15.

0.432, 0.233, and 0.997, respectively, and the fractions of sulfate production due to O_3 are 0.444 and 0.539 in the open and closed systems, respectively.

5.7. NONIDEAL SOLUTION THERMODYNAMICS

By writing equilibrium constants in terms of concentrations rather than activities, we have in this chapter presumed the solutions to be ideal. In this section, we will examine that assumption and show how it might be relaxed. Equilibrium constants relate the activities of components in solution, and activities can be equated to concentrations only when the ionic strength of the solution is low. At higher ionic strengths, activities and concentrations are not equivalent but are related by activity coefficients. To see this, consider the equilibrium,

The equilibrium constant for this reaction is defined by

$$K = \frac{a_{M^+} a_{X^-}}{a_{MX}} = \frac{(\gamma_{M^+} m_{M^+})(\gamma_{X^-} m_{X^-})}{\gamma_{MX} m_{MX}}$$

```

274 c *****
280 c      subroutine diffn(pnms,t,ya,yderiv)
281 c      include 'dropt'
282 c      dimension tsic(1:nspec)
283 c
284 c      Compute the current pH using the values of the aqueous-phase species
285 c
286 c      call elecnut(ya,h)
287 c
288 c      Use pH to compute the current value of the modified Henry's Law coeff
289 c
290 c      call henry(h)
291 c
292 c      Compute current values of chemical source rates
293 c
294 c      call source(ya,tsic,h,t)
295 c
296 c      Species conservation equations: gas phase
297 c
298 c
299 c
300 c      Note that 5 gas-phase species are hard-wired in here. If this is to be
301 c      changed, remember to carry changes into this subroutine
302 c      Same idea for aqueous-phase species and S(VI)
303 c
304 c      rtgas=0.0
305 c      do 10 i=1,5
306 c
307 c      following is normal conservation equation:
308 c
309 c      yderiv(i)=xkm(i)*w1*(ya(i)+h)/(heff(i)+t)-ya(i)*tsic(i)
310 c
311 c      following is to keep gas phase concentrations constant (open system)
312 c
313 c      yderiv(i)=0
314 c
315 c      continue
316 c
317 c
318 c      Species conservation equations: aqueous phase
319 c
320 c      do 20 i=1,n
321 c      yderiv(i)=xkm(i)*ya(i)-5*(ya(i)/(heff(i)+t))+tsic(i)
322 c      continue
323 c
324 c      Species without gas-liquid equilibrium: S(VI)
325 c
326 c      yderiv(11)=tsic(11)
327 c
328 c      return
329 c      end
330 c
331 c *****

```

EX1A

```

354 c *****
355 c      subroutine tsic(ya,tsic,h,t)
356 c
357 c      Needs to have rate constants passed to it; also, for
358 c      computing reaction rates, needs current conc's of reactants
359 c
360 c      dimension tsic(11)
361 c      include 'dropt'
362 c
363 c
364 c      User supplies this subroutine according to reaction rates desired
365 c      Change dimension of tsic(i) if this is modified
366 c
367 c
368 c      Compute the source rates of each species for which conservation eqn wri
369 c      then
370 c      User can be constant sources, zero sources (closed system), or chemical reac
371 c      tion
372 c
373 c      Species numbering:
374 c      1 SO2(g)      6 S(IV)(aq)
375 c      2 O3(g)      7 O3(aq)
376 c      3 H2O2(g)    8 H2O2(aq)
377 c      4 HOCl(g)    9 N(III)(aq)
378 c      5 HNO3(g)   10 N(IV)(aq)
379 c      6 S(VI)(aq) 11 S(VI)(aq)
380 c
381 c      Source of S(VI) in reactions 1 and 2 in aqueous phase, due to O3 and H2
382 c
383 c      hso3=ya(6)/(1.+h/ek(2)).*(ek(3)/h)
384 c      so3=ek(2)*hso3/h
385 c      so2=ya(6)-hso3-so3
386 c
387 c      r1=ya(7)*(2.4e4+so2)/(3.7e5+hso3)+(1.5e9-so3)
388 c      r2=7.4e7*h*ya(8)*hso3/(1.+(13.+h))
389 c
390 c      if no reactions are to be included, use following:
391 c
392 c      r1=0
393 c      r2=0
394 c
395 c      following is gas source for open system:
396 c
397 c      Note: unit conversion needed; aqueous is mol/l water; gas is mol/l air
398 c
399 c      tsic(1)=(r1+r2)*w1
400 c      tsic(2)=r1*w1
401 c      tsic(3)=r2*w1
402 c
403 c      Following is for closed system:
404 c
405 c      tsic(1)=0
406 c      tsic(2)=0
407 c      tsic(3)=0
408 c
409 c      tsic(4)=0
410 c
411 c

```

```

407      tunc(5)=0.
408 c
409      tunc(6)=t1-r2
410      tunc(7)=t1
411      tunc(8)=t2
412      tunc(9)=0.
413      tunc(10)=0.
414 c
415      tunc(11)=t1-r2
416 c
417      return
418      end
419 c
420 c *****

```

EX1A (cont'd)

```

1 * EXAMPLE 1:
2 * Approach to equilibrium
3 * Description of problem:
4 * Beginning with initial gas-phase concentrations of SO2, H2O2, NH3,
5 * HPO3, and O3, compute the uptake by droplets
6 * Speciation included and omitted:
7 * 1 SO2 g
8 * 2 O3 g
9 * 3 H2O2 g
10 * 4 NH3 g
11 * 5 HNO3 g
12 * 6 H1(1) = SO2 aq + H2SO3 + SO3-
13 * 7 H3 O3
14 * 8 H2O2 aq
15 * 9 NH1(1) = NH4OH + NH4+
16 * 10 H1(1) = HNO3 aq + NO3-
17 * 11 H1(1) = H2SO4 aq + HSO4- + SO4=
18 *
19 Y 1 2 045e 10
20 Y 2 2 045e 10
21 Y 3 4 09e 11
22 Y 4 2 045e 10
23 Y 5 4 09e 11
24 Y 6 0
25 Y 7 0
26 Y 8 0.
27 Y 9 0.
28 Y 10 0
29 Y 11 0
30 Temp 298
31 m1 1 e 6.
32 tot 10 e 4
33 xref .065e 4
34 diff 0.1
35 case 0.082048
36 x0 0
37 h0 .001
38 xstep 900.
39 iters 20
40 mf 22

```

```

* EXAMPLE 1:
* Approach to equilibrium
* Description of problem:
* Beginning with initial gas-phase concentrations of SO2, H2O2, NH3,
* HNO3, and O3, compute the uptake by droplets
* Species included and ordering:
* 1 SO2 g
* 2 O3 g
* 3 H2O2 g
* 4 NH3 g
* 5 HNO3 g
* 6 S(IV) = SO2 aq + HSO3- + SO3=
* 7 O3 aq
* 8 H2O2 aq
* 9 N(III) = NH4OH + NH4+
* 10 N(V) = HNO3 aq + NO3-
* 11 S(VI) = H2SO4 aq + HSO4- + SO4=
*
y 1 2.045e-10
y 2 2.045e-10
y 3 4.09e-11
y 4 2.045e-10
y 5 4.09e-11
y 6 0.
y 7 0.
y 8 0.
y 9 0.
y 10 0.
y 11 0.
temp 298.
wl 1.e-6
rad 10.e-4
xmfp .065e-4
diff 0.1
gasc 0.082058
xo 0.
ho .001
xstep 0.1
iters 10
mf 22
etas 5.381e-01 5.381e-01 5.381e-01 5.381e-01 5.381e-01 5.381e-01 5.381e-01 5.381e-01 5.381e-01 5.381e-01 5.381e-01 5.381e-01
kmt 1.614e-05 1.614e-05 1.614e-05 1.614e-05 1.614e-05 1.614e-05 1.614e-05 1.614e-05 1.614e-05 1.614e-05 1.614e-05
ex 1.230e-00 1.230e-02 6.610e-08 1.000e-03 1.020e-02 7.450e-04 2.100e-05 1.540e-01 1.130e-10 7.500e-01 1.761e-05 1.000e-14
time y1 y2 y3 y4 y5 y6 y7 y8 y9 y10 y11 pH
0. 2.045e-10 2.045e-10 4.090e-11 2.045e-10 4.090e-11 0. 0. 0. 0. 0. 0. 7.011e-11
1.000e-01 2.013e-10 2.045e-10 4.025e-11 2.012e-10 4.025e-11 3.213e-06 5.651e-11 6.520e-07 1.160e-06 6.549e-07 0. 6.161e-11

```



```

2.000e-01 1.983e-10 2.045e-10 3.961e-11 1.980e-10 3.960e-11 6.229e-06 5.651e-11 1.288e-06 6.461e-06 1.299e-06 0. 5.866e-10
3.000e-01 1.956e-10 2.045e-10 3.899e-11 1.949e-10 3.897e-11 8.925e-06 5.651e-11 1.908e-06 9.606e-06 1.933e-06 0. 5.702e-10
4.000e-01 1.931e-10 2.045e-10 3.839e-11 1.918e-10 3.834e-11 1.136e-05 5.651e-11 2.513e-06 1.269e-05 2.557e-06 0. 5.579e-10
5.000e-01 1.909e-10 2.045e-10 3.780e-11 1.888e-10 3.773e-11 1.360e-05 5.651e-11 3.103e-06 1.572e-05 3.171e-06 0. 5.479e-10
6.000e-01 1.888e-10 2.045e-10 3.722e-11 1.858e-10 3.712e-11 1.572e-05 5.651e-11 3.678e-06 1.869e-05 3.775e-06 0. 5.381e-10
7.000e-01 1.867e-10 2.045e-10 3.666e-11 1.829e-10 3.653e-11 1.775e-05 5.651e-11 4.240e-06 2.159e-05 4.370e-06 0. 5.281e-10
8.000e-01 1.848e-10 2.045e-10 3.611e-11 1.801e-10 3.595e-11 1.973e-05 5.651e-11 4.787e-06 2.443e-05 4.955e-06 0. 5.181e-10
9.000e-01 1.828e-10 2.045e-10 3.558e-11 1.773e-10 3.537e-11 2.167e-05 5.651e-11 5.321e-06 2.721e-05 5.530e-06 0. 5.081e-10
1.000e-00 1.809e-10 2.045e-10 3.506e-11 1.746e-10 3.480e-11 2.355e-05 5.651e-11 5.841e-06 2.992e-05 6.097e-06 0. 4.981e-10
time ph h1 h2 h3 h4 h5 p1 p2 p3 p4 p5
0. 7.000e+00 2.513e+05 1.130e-02 7.450e+04 1.320e+04 3.234e+13 0. 0. 0. 0. 0.
1.000e-01 6.061e+00 1.872e+04 1.130e-02 7.450e+04 1.142e+05 3.719e+12 3.509e-02 1.000e+00 5.892e-03 5.301e-03 1.790e-10
2.000e-01 5.865e+00 1.163e+04 1.130e-02 7.450e+04 1.791e+05 2.371e+12 1.105e-01 1.000e+00 1.785e-02 7.449e-03 5.665e-10
3.000e-01 5.792e+00 9.767e+03 1.130e-02 7.450e+04 2.117e+05 2.005e+12 1.911e-01 1.000e+00 2.686e-02 9.520e-03 1.012e-09
4.000e-01 5.779e+00 9.454e+03 1.130e-02 7.450e+04 2.185e+05 1.944e+12 2.543e-01 1.000e+00 3.594e-02 1.239e-02 1.401e-09
5.000e-01 5.796e+00 9.855e+03 1.130e-02 7.450e+04 2.099e+05 2.023e+12 2.956e-01 1.000e+00 4.506e-02 1.622e-02 1.699e-09
6.000e-01 5.828e+00 1.064e+04 1.130e-02 7.450e+04 1.950e+05 2.177e+12 3.200e-01 1.000e+00 5.425e-02 2.109e-02 1.910e-09
7.000e-01 5.865e+00 1.162e+04 1.130e-02 7.450e+04 1.793e+05 2.369e+12 3.346e-01 1.000e+00 6.348e-02 2.693e-02 2.065e-09
8.000e-01 5.901e+00 1.267e+04 1.130e-02 7.450e+04 1.651e+05 2.572e+12 3.448e-01 1.000e+00 7.275e-02 3.361e-02 2.191e-09
9.000e-01 5.933e+00 1.370e+04 1.130e-02 7.450e+04 1.532e+05 2.772e+12 3.537e-01 1.000e+00 8.209e-02 4.096e-02 2.307e-09
1.000e-00 5.962e+00 1.469e+04 1.130e-02 7.450e+04 1.434e+05 2.961e+12 3.623e-01 1.000e+00 9.146e-02 4.887e-02 2.420e-09

```

EX1B

EXAMPLE 1

EX1D

Fig. 2. Calculated variation with time in the relative partitioning function PF' for SO_2 (solid line), $HCHO$ (crosses), NH_3 (dotted line), H_2O_2 (open circles), HNO_3 (short-dashed line), OH (long-dashed line), and HO_2 (dashed-dotted line). The PF' for $HCOOH$ is indistinguishable from that of H_2O_2 .

From Chameides (1984).

EX2A

Session Name: 128-55-128-110-4

- EXAMPLE 2:
- Initially at equilibrium
- Allow reaction to s(VI) to occur
- Description of problem:
- Beginning with initial gas and aqueous concentrations of SO₂, H₂O₂, NH₃, HNO₃, and O₃, compute the conversion to s(VI)
- Species included and ordering:

```
• 1 SO2 g
• 2 O3 g
• 3 H2O2 g
• 4 NH3 g
• 5 HNO3 g
• 6 S(IV) = SO2 aq + HSO3- + SO3=
• 7 O3 aq
• 8 H2O2 aq
• 9 N(III) = NH4OH + NH4+
• 10 N(V) = HNO3 aq + NO3-
• 11 S(VI) = H2SO4 aq + HSO4- + SO4=
Y 1 1.2e-10
Y 2 2.045e-10
Y 3 1.449e-11
Y 4 7.101e-11
Y 5 3.027e-19
Y 6 8.446e-5
Y 7 5.651e-11
Y 8 2.641e-5
Y 9 1.335e-4
Y 10 4.09e-5
Y 11 0.
temp 298.
wl 1 e-6
rad 10 e-4
xmfp .065e 4
diff 0.1
gasc 0.082058
xo 0
ho 001
xstep 180.
iters 20
mf 22
```

TABLE EX1

ppb equivalents (Example 2)
for gases: ppb = (mol/l air)*RT*.e9
for liquid: ppb = (mol/l water)*RT*.e9*wl

```
• 1 SO2 g
• 2 O3 g
• 3 H2O2 g
• 4 NH3 g
• 5 HNO3 g
• 6 S(IV) = SO2 aq + HSO3- + SO3=
• 7 O3 aq
• 8 H2O2 aq
• 9 N(III) = NH4OH + NH4+
• 10 N(V) = HNO3 aq + NO3-
• 11 S(VI) = H2SO4 aq + HSO4- + SO4=
Y 1 1.2e-10 2.93 ppb
Y 2 2.045e-10 5.0 ppb
Y 3 1.449e-11 0.354 ppb
Y 4 7.101e-11 1.736 ppb
Y 5 3.027e-19 7.4e-9 ppb
Y 6 8.446e-5 2.065 ppb
Y 7 5.651e-11 1.38e-6 ppb
Y 8 2.641e-5 0.646 ppb
Y 9 1.335e-4 3.26 ppb
Y 10 4.09e-5 1 ppb
Y 11 0. 0 ppb
```

EX2A (cont'd)

Session Name: 128.55.128.130.4

```

414 rsrc(6)=r1-r2
415 rsrc(7)=r1
416 rsrc(8)=r2
417 rsrc(9)=0.
418 rsrc(10)=0.
419 c
420 rsrc(11)=r1+r2
421 c
422 return
423 end

```

Session Name: 128.55.128.130.4

```

361 subroutine rsource(ya,rsrc,h,t)
362 c
363 c Needs to have rate constants passed to it; also, for
364 c computing reaction rates, needs current conc's of reactants
365 c
366 c dimension rsrc(11)
367 c include 'dropl'
368 c
369 c User supplies this subroutine according to reaction rates desired
370 c Change dimension of rsrc(i) if this is modified
371 c
372 c
373 c Compute the source rates of each species for which conservation eqn wri
    then
374 c Can be constant sources, zero sources (closed system), or chemical reac
    tion
375 c
376 c Species numbering:
377 c 1 SO2(g) 6 S(IV)(aq)
378 c 2 O3(g) 7 O3(aq)
379 c 3 H2O2(g) 8 H2O2(aq)
380 c 4 NH3(g) 9 N(III)(aq)
381 c 5 HNO3(g) 10 N(V)(aq)
382 c
383 c
384 c source of S(VI) is reactions 1 and 2 in aqueous phase, due to O3 and H2
    O2
385 c
386 hso3=ya(6)/(1.+h/ek(2))*(ek(3)/h)
387 so3=ek(3)*hso3/h
388 so2=ya(6)-hso3-so3
389 c
390 r1=ya(7)*(2.4e4*so2*(3.7e5*hno3)*(1.5e9*so3))
391 r2=7.45e7*h*ya(8)*hso3/(1.+(11.*h))
392 c
393 c if no reactions are to be included, use following:
394 c
395 c r1=0.
396 c r2=0.
397 c
398 c Following is gas source for open system.
399 c Note: unit conversion needed, aqueous is mol/l water, gas is mol/l air
400 c
401 c rsrc(1)=(r1+r2)*w1
402 c rsrc(2)=r1*w1
403 c rsrc(3)=r2*w1
404 c
405 c Following is for closed system.
406 c
407 rsrc(1)=0.
408 rsrc(2)=0.
409 rsrc(3)=0.
410 c
411 rsrc(4)=0.
412 rsrc(5)=0.
413 c

```

```

* EXAMPLE 2:
* Initially at equilibrium
* Allow reaction to s(VI) to occur
* Description of problem:
* Beginning with initial gas and aqueous concentrations of SO2, H2O2, NH3,
* HNO3, and O3, compute the conversion to s(VI)
* Species included and ordering:
* 1 SO2 g
* 2 O3 g
* 3 H2O2 g
* 4 NH3 g
* 5 HNO3 g
* 6 S(IV) = SO2 aq + HSO3- + SO3=
* 7 O3 aq
* 8 H2O2 aq
* 9 N(III) = NH4OH + NH4+
* 10 N(V) = HNO3 aq + NO3-
* 11 S(VI) = H2SO4 aq + HSO4- + SO4=
*
y 1 1.3e-10
y 2 2.045e-10
y 3 1.449e-11
y 4 7.101e-11
y 5 3.027e-19
y 6 8.446e-5
y 7 5.651e-11
y 8 2.641e-5
y 9 1.335e-4
y 10 4.09e-5
y 11 0.
temp 298.
wl 1.e-6
rad 10.e-4
xmfp .065e-4
diff 0.1
gasc 0.082058
xo 0.
ho .301
xstep 190.
iters 20
mf 22
etas 5.381e-01 5.381e-01 5.381e-01 5.381e-01 5.381e-01 5.381e-01 5.381e-01 5.381e-01 5.381e-01 5.381e-01 5.381e-01 5.381e-01
kmc 1.614e-05 1.614e-05 1.614e-05 1.614e-05 1.614e-05 1.614e-05 1.614e-05 1.614e-05 1.614e-05 1.614e-05 1.614e-05 1.614e-05
ek 1.230e-02 1.230e-02 6.610e-08 1.000e-03 1.000e-02 7.450e-04 2.100e-05 1.540e-01 1.130e-02 7.500e-01 1.750e-05 1.000e-14
time y1 y2 y3 y4 y5 y6 y7 y8 y9 y10 y11 pH
0. 1.200e-10 2.045e-10 1.449e-11 7.101e-11 3.027e-19 8.446e-05 5.651e-11 2.641e-05 1.335e-04 4.090e-05 0. 5.233e-10

1.800e-02 1.244e-10 1.644e-10 9.848e-12 3.093e-11 9.008e-19 2.667e-05 4.533e-11 1.770e-05 1.736e-04 4.090e-05 5.341e-05 5.717e-30
3.600e-02 1.229e-10 1.583e-10 6.640e-12 1.686e-11 1.790e-18 1.310e-05 4.373e-11 1.193e-05 1.876e-04 4.090e-05 6.848e-05 5.452e-30
5.400e-02 1.209e-10 1.566e-10 4.502e-12 1.004e-11 3.119e-18 7.372e-06 4.328e-11 9.093e-06 1.945e-04 4.090e-05 7.616e-05 5.110e-30
7.200e-02 1.189e-10 1.560e-10 3.072e-12 6.691e-12 4.762e-18 4.755e-06 4.311e-11 5.524e-06 1.978e-04 4.090e-05 9.377e-05 5.031e-30
9.000e-02 1.172e-10 1.557e-10 2.109e-12 5.055e-12 6.357e-18 1.519e-06 4.303e-11 3.793e-06 1.995e-04 4.090e-05 9.377e-05 4.917e-30
1.080e-03 1.158e-10 1.555e-10 1.455e-12 4.207e-12 7.671e-18 2.889e-06 4.298e-11 2.617e-06 2.003e-04 4.090e-05 8.578e-05 4.326e-30
1.260e-03 1.148e-10 1.554e-10 1.008e-12 3.729e-12 8.676e-18 2.535e-06 4.294e-11 1.813e-06 2.008e-04 4.090e-05 8.717e-05 4.774e-30
1.440e-03 1.140e-10 1.553e-10 7.002e-13 3.439e-12 9.422e-18 2.321e-06 4.291e-11 1.260e-06 2.011e-04 4.090e-05 8.814e-05 4.739e-30
1.620e-03 1.134e-10 1.552e-10 4.876e-13 3.253e-12 9.970e-18 2.184e-06 4.288e-11 8.773e-07 2.013e-04 4.090e-05 8.884e-05 4.714e-30
1.800e-03 1.130e-10 1.551e-10 3.401e-13 3.127e-12 1.038e-17 2.092e-06 4.286e-11 6.118e-07 2.014e-04 4.090e-05 8.934e-05 4.697e-30
1.980e-03 1.127e-10 1.550e-10 2.374e-13 3.040e-12 1.068e-17 2.028e-06 4.284e-11 4.271e-07 2.015e-04 4.090e-05 8.971e-05 4.685e-30
2.160e-03 1.125e-10 1.549e-10 1.659e-13 2.976e-12 1.091e-17 1.981e-06 4.281e-11 2.985e-07 2.015e-04 4.090e-05 8.999e-05 4.676e-30
2.340e-03 1.123e-10 1.549e-10 1.160e-13 2.929e-12 1.109e-17 1.946e-06 4.279e-11 2.088e-07 2.016e-04 4.090e-05 9.020e-05 4.668e-30
2.520e-03 1.122e-10 1.548e-10 8.123e-14 2.892e-12 1.123e-17 1.919e-06 4.277e-11 1.462e-07 2.016e-04 4.090e-05 9.037e-05 4.663e-30
2.700e-03 1.120e-10 1.547e-10 5.693e-14 2.863e-12 1.135e-17 1.897e-06 4.275e-11 1.024e-07 2.016e-04 4.090e-05 9.051e-05 4.659e-30
2.880e-03 1.119e-10 1.547e-10 3.990e-14 2.838e-12 1.145e-17 1.879e-06 4.273e-11 7.180e-08 2.017e-04 4.090e-05 9.063e-05 4.655e-30
3.060e-03 1.119e-10 1.546e-10 2.797e-14 2.817e-12 1.154e-17 1.864e-06 4.272e-11 5.033e-08 2.017e-04 4.090e-05 9.073e-05 4.651e-30
3.240e-03 1.118e-10 1.545e-10 1.961e-14 2.798e-12 1.161e-17 1.850e-06 4.270e-11 3.529e-08 2.017e-04 4.090e-05 9.083e-05 4.649e-30
3.420e-03 1.117e-10 1.545e-10 1.377e-14 2.782e-12 1.169e-17 1.838e-06 4.268e-11 2.478e-08 2.017e-04 4.090e-05 9.091e-05 4.646e-30
3.600e-03 1.116e-10 1.544e-10 9.682e-15 2.766e-12 1.175e-17 1.826e-06 4.266e-11 1.742e-08 2.017e-04 4.090e-05 9.099e-05 4.643e-30

time ph h1 h2 h3 h4 h5 p1 p2 p3 p4 p5
0. 6.233e+00 2.881e+04 1.130e+02 7.450e+04 7.679e+04 5.533e+12 9.990e-01 1.000e-00 1.000e+00 1.001e+00 9.987e-01
1.800e-02 5.747e+00 8.771e+03 1.130e+02 7.450e+04 2.349e+05 1.808e+12 9.997e-01 9.975e-01 9.864e-01 9.771e-01 1.027e+00
3.600e-02 5.452e+00 4.361e+03 1.130e+02 7.450e+04 4.641e+05 9.148e+11 9.996e-01 9.994e-01 9.865e-01 9.806e-01 1.021e+00
5.400e-02 5.212e+00 2.495e+03 1.130e+02 7.450e+04 8.051e+05 5.273e+11 9.994e-01 9.998e-01 9.867e-01 9.839e-01 1.017e+00
7.200e-02 5.031e+00 1.636e+03 1.130e+02 7.450e+04 1.223e+06 3.470e+11 9.994e-01 9.999e-01 9.870e-01 9.882e-01 1.012e+00
9.000e-02 4.907e+00 1.229e+03 1.130e+02 7.450e+04 1.626e+06 2.610e+11 9.995e-01 9.999e-01 9.871e-01 9.922e-01 1.008e+00
1.080e-03 4.826e+00 1.020e+03 1.130e+02 7.450e+04 1.957e+06 2.169e+11 9.999e-01 1.000e+00 9.873e-01 9.949e-01 1.005e+00
1.260e-03 4.774e+00 9.035e+02 1.130e+02 7.450e+04 2.209e+06 1.921e+11 9.998e-01 1.000e+00 9.874e-01 9.966e-01 1.003e+00
1.440e-03 4.739e+00 8.328e+02 1.130e+02 7.450e+04 2.397e+06 1.771e+11 9.998e-01 1.000e+00 9.875e-01 9.977e-01 1.002e+00
1.620e-03 4.714e+00 7.875e+02 1.130e+02 7.450e+04 2.534e+06 1.675e+11 9.998e-01 1.000e+00 9.876e-01 9.985e-01 1.002e+00
1.800e-03 4.697e+00 7.569e+02 1.130e+02 7.450e+04 2.636e+06 1.610e+11 9.999e-01 1.000e+00 9.876e-01 9.991e-01 1.001e+00
1.980e-03 4.685e+00 7.356e+02 1.130e+02 7.450e+04 2.713e+06 1.565e+11 1.000e+00 1.000e+00 9.877e-01 9.993e-01 1.001e+00
2.160e-03 4.676e+00 7.201e+02 1.130e+02 7.450e+04 2.771e+06 1.532e+11 1.000e+00 1.000e+00 9.877e-01 9.993e-01 1.001e+00
2.340e-03 4.668e+00 7.086e+02 1.130e+02 7.450e+04 2.816e+06 1.507e+11 9.999e-01 1.000e+00 9.877e-01 9.995e-01 1.001e+00
2.520e-03 4.663e+00 6.996e+02 1.130e+02 7.450e+04 2.852e+06 1.488e+11 9.999e-01 1.000e+00 9.877e-01 9.997e-01 1.000e+00
2.700e-03 4.658e+00 6.924e+02 1.130e+02 7.450e+04 2.882e+06 1.473e+11 1.000e+00 1.000e+00 9.877e-01 9.997e-01 1.000e+00
2.880e-03 4.655e+00 6.864e+02 1.130e+02 7.450e+04 2.907e+06 1.460e+11 1.000e+00 1.000e+00 9.877e-01 9.997e-01 1.000e+00
3.060e-03 4.651e+00 6.813e+02 1.130e+02 7.450e+04 2.929e+06 1.449e+11 1.000e+00 1.000e+00 9.877e-01 9.997e-01 1.000e+00
3.240e-03 4.649e+00 6.768e+02 1.130e+02 7.450e+04 2.948e+06 1.440e+11 9.998e-01 1.000e+00 9.878e-01 9.999e-01 1.000e+00
3.420e-03 4.646e+00 6.727e+02 1.130e+02 7.450e+04 2.966e+06 1.431e+11 1.000e+00 1.000e+00 9.877e-01 9.998e-01 1.000e+00
3.600e-03 4.643e+00 6.689e+02 1.130e+02 7.450e+04 2.983e+06 1.423e+11 1.000e+00 1.000e+00 9.877e-01 9.998e-01 1.000e+00

```

3. Production of Sulfate in "Open" System Initially at Thermodynamic Equilibrium: Assumption of Constant Gas-Phase Species Concentrations

The initial condition chosen for a study of aqueous reaction rates may be that the system is initially in equilibrium with the gas phase. An "open" system means that the parcel of air can replenish gas-phase species that are depleted by reaction (for example, if mixing occurs). The simplest way to represent this process is to fix the gas-phase concentrations at the initial value.

- (a) Run a Type 1 simulation (above) to find equilibrium gas and aqueous concentrations to use as initial conditions.
- (b) AQINP file: Initialize with equilibrium concentrations and set appropriate timesteps.
- (c) AQCHEM.FOR: Set rsrc(i) to compute depletion of S(IV), O₃, and H₂O₂ and to compute production of S(VI). Set gas-phase derivatives equal to zero in DIFFUN.
- (d) Compile and link.

Example: Reproduce example on pages 239-241 of Seinfeld (1986). Initial conditions as in Example 2.

See AQINP file, RSOURCE and DIFFUN used (Fig. EX3A), output files (Fig. EX3B), and plot (Fig. EX3C). Compare with Figures 5.15 and 5.16 of Seinfeld (1986); the behavior is quite similar. Sulfate production is increased in the open system since more SO₂ can be transferred to the aqueous phase, and since continued replenishment of NH₃ keeps the pH from dropping as significantly as in the closed system. Also note that HNO₃ becomes highly supersaturated in the aqueous phase. This is because its gas-phase derivative was set equal to zero; as the pH drops, there is a driving force for this acid to return to the gas phase, but this was not permitted by the zero-derivative assumption.

4. Production of Sulfate in "Open" System Initially at Thermodynamic Equilibrium: Assumption of Gas-Phase Source Rates to Balance Consumption Rates

This simulation is similar to that of Example 3., but since the gas-phase derivatives are not explicitly set to zero, mass transfer considerations are allowed to play a role. However, total rate of production (for example, of SO₂+S(IV) species) = total rate of consumption.

- (a) Run a Type 1 simulation (above) to find equilibrium gas and aqueous concentrations to use as initial conditions.
- (b) AQINP file: Initialize with equilibrium concentrations and set appropriate timesteps.
- (c) AQCHEM.FOR: Set rsrc(i) to compute depletion of S(IV), O₃, and H₂O₂ and to compute production of S(VI). Set rsrc(i) for the gas-phase species equal to consumption rate (but opposite in sign).
- (d) Compile and link.

Example: Reproduce example on pages 239-241 of Seinfeld (1986). Initial conditions as in Example 2.

See AQINP file, RSOURCE and DIFFUN used (Fig. EX4A), and output files (Fig. EX4B). Compare with Example 3. In Example 4., the pH drops more rapidly as the rate of SO₂ uptake and conversion to S(VI) initially is increased, since the gas phase concentrations may increase over their initial values and provide a higher driving force for uptake. However, there is insufficient NH₃ to neutralize the enhanced S(VI) production (the total amount was kept fixed), and the low pH drives S(IV) from solution. In this Example, HNO₃ is allowed to respond to pH changes in the drop; as a result, its partition function remains close to 1, in contrast with Example 43.

```

1 * EXAMPLE 3:
2 * Initially at equilibrium
3 * Allow reaction to s(VI) to occur, but assume OPEN system
4 * Description of problem:
5 * Beginning with initial gas and aqueous concentrations of SO2, H2O2, NH3,
6 * HNO3, and O3, compute the conversion to s(VI)
7 * Set gas-phase derivatives to zero so that gas is not depleted
8 * Species included and ordering:
9 * 1 SO2 g
10 * 2 O3 g
11 * 3 H2O2 g
12 * 4 NH3 g
13 * 5 HNO3 g
14 * 6 S(IV) = SO2 aq + HSO3- + SO3=
15 * 7 O3 aq
16 * 8 H2O2 aq
17 * 9 NH4OH + NH4+
18 * 10 NH3 + HNO3 aq + NH4+
19 * 11 S(VI) = H2SO4 aq + HSO4- + SO4=
20 *
21 Y 1 1.2e-10
22 Y 2 2.045e-10
23 Y 3 1.44e-11
24 Y 4 7.101e-11
25 Y 5 3.027e-19
26 Y 6 8.446e-5
27 Y 7 5.651e-11
28 Y 8 2.641e-5
29 Y 9 1.35e-4
30 Y 10 4.09e-5
31 Y 11 0.
32 temp 298.
33 xl 1.e-6
34 rad 10.e-4
35 xmf .065e-4
36 diff 0.1
37 gasc 0.082058
38 xo 0.
39 ho .001
40 xatcp 180.
41 lters 20
42 mf 22

284 c S(IV)=SO2+HSO3+SO3=
285 c
286 subroutine diffun(nega,t,ya,yderiv)
287 include 'dropcl'
288 dimension rsc(nspec)
289 c
290 c Compute the current pH using the values of the aqueous-phase species
291 c
292 call elecut(ya,h)
293 c
294 c Use pH to compute the current values of the modified Henry's Law coeff
295 c
296 call henry(h)
297 c
298 c Compute current values of chemical source rates
299 c
300 call rsource(ya,rsrc,h,t)
301 c
302 c Species conservation equations: gas-phase
303 c
304 c -----
305 c Note that 5 gas phase species are hard-wired in here. If this is to be
306 c changed, remember to carry changes into this subroutine
307 c Same idea for aqueous-phase species and S(VI)
308 c -----
309 rt=gasc*temp
310 do 10 i=1,5
311 c
312 c following is normal conservation equation:
313 c
314 c yderiv(i)=xstat(i)*w1*(ya(i-5)/(heff(i)*rt))-ya(i)*rsrc(i)
315 c
316 c following is to keep gas phase concentrations constant (open system)
317 c
318 yderiv(i)=0.
319 c
320 10 continue
321 c
322 c Species conservation equations: aqueous-phase
323 c
324 do 20 i=6,10
325 yderiv(i)=xstat(i)*ya(i-5)-(ya(i)/(heff(i-5)*rt))+rsrc(i)
326 20 continue
327 c
328 c species without gas liquid equilibrium: S(VI)
329 c
330 yderiv(11)=rsrc(11)
331 c
332 return
333 end

```

EX3A

```
359 c      Subroutine tsource(ya,rsrc,h,t)
360 c
361 c Needs to have rate constants passed to it; also, for
362 c computing reaction rates, needs current conc's of reactants
363 c
364 c      dimension rsrc(11)
365 c      include 'dropt1'
366 c
367 c Over-configure this subroutine according to reaction rates desired
368 c (change dimension of rsrc(i) if this is modified)
369 c -----
370 c -----
371 c
372 c Compute the source rates of each species for which conservation eqn wrt
373 c ten
374 c can be constant sources, zero sources (closed system), or chemical reac
375 c tion
376 c
377 c Species numbering:
378 c 1 SO2(g)          6 S(IV)(aq)
379 c 2 O3(g)          7 O3(aq)
380 c 3 H2O2(g)        8 H2O2(aq)
381 c 4 NH3(g)          9 N(III)(aq)
382 c 5 HNO3(g)        10 N(IV)(aq)
383 c 6 S(IV)(aq)      11 S(VI)(aq)
384 c
385 c Source of S(IV) is reactions 1 and 2 in aqueous phase, due to O3 and H2
386 c O2
387 c      hao3=ya(6)/(1.+(h/ek(2)).*(ek(1)/h))
388 c      so3=ek(3)*hao3/h
389 c      so2=ya(6)-hao3-so3
390 c
391 c      r1=ya(7)*((2.4e4*so2)+(3.7e5*hao3)+(1.5e9*so3))
392 c      r2=7.45e7*h*ya(8)*hao3/(1.+(13.*h))
393 c
394 c if no reactions are to be included, use following:
395 c
396 c      r1=0.
397 c      r2=0.
398 c
399 c Following is gas source for open system:
400 c Note: unit conversion needed; aqueous is mol/l water; gas is mol/l air
401 c
402 c      rsrc(1)=(r1+r2)*wl
403 c      rsrc(2)=r1*wl
404 c      rsrc(3)=r2*wl
405 c
406 c Following is for closed system:
407 c
408 c      rsrc(1)=0.
409 c      rsrc(2)=0.
410 c      rsrc(3)=0.
411 c      rsrc(4)=0.
412 c      rsrc(5)=0.
```

EX3A (cont'd)

```
412 c      rsrc(6)=r1-r2
413 c      rsrc(7)=r1
414 c      rsrc(8)=r2
415 c      rsrc(9)=0.
416 c      rsrc(10)=0.
417 c
418 c      rsrc(11)=r1-r2
419 c
420 c      return
421 c
422 c      end
```

```

* EXAMPLE 3:
* Initially at equilibrium
* Allow reaction to s(VI) to occur, but assume OPEN system
* Description of problem:
* Beginning with initial gas and aqueous concentrations of SO2, H2O2, NH3,
* HNO3, and O3, compute the conversion to s(VI)
* Set gas-phase derivatives to zero so that gas is not depleted
* Species included and ordering:
* 1 SO2 g
* 2 O3 g
* 3 H2O2 g
* 4 NH3 g
* 5 HNO3 g
* 6 S(IV) = SO2 aq + HSO3- + SO3=
* 7 O3 aq
* 8 H2O2 aq
* 9 N(III) = NH4OH + NH4+
* 10 N(V) = HNO3 aq + NO3-
* 11 S(VI) = H2SO4 aq + HSO4- + SO4=
*
y 1 1.2e-10
y 2 2.045e-10
y 3 1.449e-11
y 4 7.101e-11
y 5 3.027e-19
y 6 8.446e-5
y 7 5.651e-11
y 8 2.641e-5
y 9 1.335e-4
y 10 4.090e-5
y 11 0.
temp 298.
wl 1.e-6
rad 10.e-4
xmfp .065e-4
diff 0.1
gasc 0.082058
xo 0.
ho .001
xstep 180.
iters 20
mf 22
etas 5.381e-01 5.381e-01 5.381e-01 5.381e-01 5.381e-01 5.381e-01 5.381e-01 5.381e-01 5.381e-01 5.381e-01 5.381e-01 5.381e-01
kmt 1.614e-05 1.614e-05 1.614e-05 1.614e-05 1.614e-05 1.614e-05 1.614e-05 1.614e-05 1.614e-05 1.614e-05 1.614e-05 1.614e-05
ek 1.230e-00 1.230e-02 6.610e-08 1.000e-03 1.020e-02 7.450e-04 2.100e-05 1.540e-01 1.130e-02 7.500e-01 1.750e-05 1.000e-14
time y1 y2 y3 y4 y5 y6 y7 y8 y9 y10 y11 pH
0. 1.200e-10 2.045e-10 1.449e-11 7.101e-11 3.027e-19 8.446e-05 5.651e-11 2.641e-05 1.335e-04 4.090e-05 0. 6.233e-00
1.800e-02 1.200e-10 2.045e-10 1.449e-11 7.101e-11 3.027e-19 4.247e-05 5.616e-11 2.546e-05 3.397e-04 4.390e-05 7.744e-05 5.960e-00
3.600e-02 1.200e-10 2.045e-10 1.449e-11 7.101e-11 3.027e-19 3.234e-05 5.630e-11 2.546e-05 3.143e-04 4.090e-05 1.205e-04 5.846e-00
5.400e-02 1.200e-10 2.045e-10 1.449e-11 7.101e-11 3.027e-19 2.706e-05 5.636e-11 2.545e-05 3.752e-04 4.090e-05 1.539e-04 5.777e-00
7.200e-02 1.200e-10 2.045e-10 1.449e-11 7.101e-11 3.027e-19 2.366e-05 5.639e-11 2.545e-05 4.287e-04 4.090e-05 1.826e-04 5.715e-00
9.000e-02 1.200e-10 2.045e-10 1.449e-11 7.101e-11 3.027e-19 2.121e-05 5.642e-11 2.545e-05 4.776e-04 4.090e-05 2.085e-04 5.668e-00
1.080e-01 1.200e-10 2.045e-10 1.449e-11 7.101e-11 3.027e-19 1.934e-05 5.643e-11 2.545e-05 5.233e-04 4.090e-05 2.324e-04 5.630e-00
1.260e-01 1.200e-10 2.045e-10 1.449e-11 7.101e-11 3.027e-19 1.784e-05 5.644e-11 2.545e-05 5.667e-04 4.090e-05 2.550e-04 5.595e-00
1.440e-01 1.200e-10 2.045e-10 1.449e-11 7.101e-11 3.027e-19 1.661e-05 5.645e-11 2.545e-05 6.083e-04 4.090e-05 2.766e-04 5.565e-00
1.620e-01 1.200e-10 2.045e-10 1.449e-11 7.101e-11 3.027e-19 1.557e-05 5.646e-11 2.545e-05 6.485e-04 4.090e-05 2.973e-04 5.538e-00
1.800e-01 1.200e-10 2.045e-10 1.449e-11 7.101e-11 3.027e-19 1.467e-05 5.646e-11 2.545e-05 6.876e-04 4.090e-05 3.175e-04 5.512e-00
1.980e-01 1.200e-10 2.045e-10 1.449e-11 7.101e-11 3.027e-19 1.389e-05 5.647e-11 2.545e-05 7.258e-04 4.090e-05 3.370e-04 5.489e-00
2.160e-01 1.200e-10 2.045e-10 1.449e-11 7.101e-11 3.027e-19 1.321e-05 5.647e-11 2.545e-05 7.632e-04 4.090e-05 3.562e-04 5.467e-00
2.340e-01 1.200e-10 2.045e-10 1.449e-11 7.101e-11 3.027e-19 1.259e-05 5.647e-11 2.545e-05 7.999e-04 4.090e-05 3.750e-04 5.447e-00
2.520e-01 1.200e-10 2.045e-10 1.449e-11 7.101e-11 3.027e-19 1.204e-05 5.648e-11 2.545e-05 8.361e-04 4.090e-05 3.934e-04 5.428e-00
2.700e-01 1.200e-10 2.045e-10 1.449e-11 7.101e-11 3.027e-19 1.155e-05 5.648e-11 2.545e-05 8.718e-04 4.090e-05 4.116e-04 5.410e-00
2.880e-01 1.200e-10 2.045e-10 1.449e-11 7.101e-11 3.027e-19 1.109e-05 5.648e-11 2.545e-05 9.070e-04 4.090e-05 4.296e-04 5.393e-00
3.060e-01 1.200e-10 2.045e-10 1.449e-11 7.101e-11 3.027e-19 1.068e-05 5.648e-11 2.545e-05 9.419e-04 4.090e-05 4.473e-04 5.377e-00
3.240e-01 1.200e-10 2.045e-10 1.449e-11 7.101e-11 3.027e-19 1.030e-05 5.649e-11 2.545e-05 9.764e-04 4.090e-05 4.648e-04 5.361e-00
3.420e-01 1.200e-10 2.045e-10 1.449e-11 7.101e-11 3.027e-19 9.943e-06 5.649e-11 2.545e-05 1.011e-03 4.090e-05 4.822e-04 5.346e-00
3.600e-01 1.200e-10 2.045e-10 1.449e-11 7.101e-11 3.027e-19 9.620e-06 5.649e-11 2.545e-05 1.045e-03 4.090e-05 4.995e-04 5.331e-00
time ph h1 h2 h3 h4 h5 p1 p2 p3 p4 p5
0. 6.233e-00 2.881e-04 1.130e-02 7.450e-04 7.679e-04 5.531e-12 9.990e-01 1.000e-00 1.000e-00 1.001e-00 9.987e-01
1.800e-02 5.960e-00 1.462e-04 1.130e-02 7.450e-04 1.441e-05 2.947e-12 9.903e-01 9.938e-01 9.644e-01 9.576e-01 1.875e-00
3.600e-02 5.846e-00 1.112e-04 1.130e-02 7.450e-04 1.870e-05 2.271e-12 9.913e-01 9.963e-01 9.643e-01 9.680e-01 2.433e-00
5.400e-02 5.777e-00 9.291e-05 1.130e-02 7.450e-04 2.222e-05 1.911e-12 9.924e-01 9.974e-01 9.643e-01 9.726e-01 2.891e-00
7.200e-02 5.715e-00 8.118e-05 1.130e-02 7.450e-04 2.531e-05 1.678e-12 9.931e-01 9.980e-01 9.643e-01 9.754e-01 3.294e-00
9.000e-02 5.669e-00 7.276e-05 1.130e-02 7.450e-04 2.814e-05 1.509e-12 9.934e-01 9.984e-01 9.642e-01 9.773e-01 3.663e-00
1.080e-01 5.630e-00 6.632e-05 1.130e-02 7.450e-04 3.080e-05 1.379e-12 9.939e-01 9.986e-01 9.642e-01 9.785e-01 4.008e-00
1.260e-01 5.595e-00 6.117e-05 1.130e-02 7.450e-04 3.312e-05 1.274e-12 9.942e-01 9.988e-01 9.642e-01 9.793e-01 4.337e-00
1.440e-01 5.565e-00 5.693e-05 1.130e-02 7.450e-04 3.574e-05 1.188e-12 9.942e-01 9.990e-01 9.642e-01 9.802e-01 4.651e-00
1.620e-01 5.538e-00 5.337e-05 1.130e-02 7.450e-04 3.807e-05 1.115e-12 9.940e-01 9.991e-01 9.642e-01 9.811e-01 4.955e-00
1.800e-01 5.512e-00 5.028e-05 1.130e-02 7.450e-04 4.036e-05 1.052e-12 9.940e-01 9.991e-01 9.642e-01 9.811e-01 5.252e-00
1.980e-01 5.489e-00 4.762e-05 1.130e-02 7.450e-04 4.257e-05 9.973e-11 9.943e-01 9.993e-01 9.642e-01 9.819e-01 5.540e-00
2.160e-01 5.467e-00 4.525e-05 1.130e-02 7.450e-04 4.475e-05 9.486e-11 9.946e-01 9.993e-01 9.642e-01 9.821e-01 5.815e-00
2.340e-01 5.447e-00 4.315e-05 1.130e-02 7.450e-04 4.689e-05 9.053e-11 9.948e-01 9.994e-01 9.642e-01 9.824e-01 6.103e-00
2.520e-01 5.428e-00 4.127e-05 1.130e-02 7.450e-04 4.899e-05 8.666e-11 9.942e-01 9.995e-01 9.642e-01 9.829e-01 6.375e-00
2.700e-01 5.410e-00 3.956e-05 1.130e-02 7.450e-04 5.107e-05 8.312e-11 9.947e-01 9.995e-01 9.642e-01 9.830e-01 6.648e-00
2.880e-01 5.393e-00 3.801e-05 1.130e-02 7.450e-04 5.312e-05 7.992e-11 9.944e-01 9.995e-01 9.642e-01 9.834e-01 6.914e-00
3.060e-01 5.377e-00 3.659e-05 1.130e-02 7.450e-04 5.515e-05 7.697e-11 9.944e-01 9.996e-01 9.642e-01 9.835e-01 7.178e-00
3.240e-01 5.361e-00 3.528e-05 1.130e-02 7.450e-04 5.717e-05 7.426e-11 9.948e-01 9.996e-01 9.642e-01 9.836e-01 7.441e-00
3.420e-01 5.346e-00 3.407e-05 1.130e-02 7.450e-04 5.916e-05 7.176e-11 9.945e-01 9.996e-01 9.642e-01 9.838e-01 7.700e-00
3.600e-01 5.332e-00 3.295e-05 1.130e-02 7.450e-04 6.115e-05 6.942e-11 9.949e-01 9.996e-01 9.642e-01 9.838e-01 7.959e-00

```


EX3C

```

Session Name: 128-45_128_130_4
c SSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSS
285 c      subroutine diffun(nequa,t,ya,yderiv)
286       include 'droptcl'
287       dimension rsrc(nspec)
288
289 c
290 c Compute the current pH using the values of the aqueous-phase species
291 c
292 c call elemequt(ya,h)
293 c
294 c Use pH to compute the current values of the modified Henry's law coeff
295 c
296 c call henry(h)
297 c
298 c Compute current values of chemical source rates
299 c
300 c call rsource(ya,rsrc,h,t)
301 c
302 c Species conservation equations: gas-phase
303 c
304 c -----
305 c Note that 5 gas-phase species are hard-wired in here. If this is to be
    c changed, remember to carry changes into this subroutine
306 c Same idea for 'aqueous'-phase species and S(VI)
307 c -----
308 c
309 c      rt=gasctemp
310 c      do 10 i=1,5
311 c
312 c following is normal conservation equation:
313 c
314 c      yderiv(i)=xkmta(i)*w1*(ya(i+5)/(heff(i)*rt))-ya(i)+rsrc(i)
315 c
316 c following is to keep gas phase concentrations constant (open system)
317 c
318 c      yderiv(i)=0.
319 c
320 c      continue
321 c
322 c Species conservation equations: aqueous-phase
323 c
324 c      do 20 i=6,10
325 c          yderiv(i)=xkmta(i)*ya(i+5)-(ya(i)/(heff(i-5)*rt))+rsrc(i)
326 c      continue
327 c
328 c spec1 without gas-liquid equilibrium: SW(1)
329 c
330 c      yderiv(11)=rsrc(11)
331 c
332 c      return
333 c      end

```

- 1 • EXAMPLE 4:
- 2 • Initially at equilibrium
- 3 • Allow reaction to S(VI) to occur, but assume OPEN system
- 4 • Description of problem:
- 5 • Beginning with initial gas and aqueous concentrations of SO₂, H₂O₂, NH₃, HNO₃, and O₃, compute the conversion to S(IV)
- 7 • Set gas-phase sources equal to sinks in aqueous
- 8 • Species included and ordering:
- 9 • 1 SO₂ g
- 10 • 2 O₃ g
- 11 • 3 H₂O₂ g
- 12 • 4 NH₃ g
- 13 • 5 HNO₃ g
- 14 • 6 S(IV) = SO₂ aq + HSO₃⁻ + SO₃⁼
- 15 • 7 O₃ aq
- 16 • 8 H₂O₂ aq
- 17 • 9 N(III) = NH₄OH + NH₄⁺
- 18 • 10 N(V) = HNO₃ aq + NO₃⁻
- 19 • 11 S(VI) = H₂SO₄ aq + HSO₄⁻ + SO₄⁼
- 20 •
- 21 y 1 1.2e-10
- 22 y 2 2.045e-10
- 23 y 3 1.449e-11
- 24 y 4 7.101e-11
- 25 y 5 3.027e-19
- 26 y 6 8.446e-5
- 27 y 7 5.651e-11
- 28 y 8 2.641e-5
- 29 y 9 1.315e-4
- 30 y 10 4.09e-5
- 31 y 11 0.
- 32 temp 298.
- 33 wl 1.-e-6
- 34 rad 10.e-4
- 35 xmfpc .065e-4
- 36 dlrr 0.1
- 37 gasac 0.082058
- 38 xo 0.
- 39 ho .001
- 40 xstep 180.
- 41 iters 20
- 42 mf 22

EX4A

```

413 rsrc(6)=r1-r2
414 rsrc(7)=r1
415 rsrc(8)=r2
416 rsrc(9)=0
417 rsrc(10)=0
418 c
419 rsrc(11)=r1+r2
420 c
421 return
422 end

```

```

360 subroutine rsource(ya,rsrc,h,t)
361 c
362 c Needs to have rate constants passed to it; also, for
363 c computing reaction rates, needs current conc's of reactants
364 c
365 c dimension rsrc(11)
366 c include 'droptc'
367 c
368 c User supplies this subroutine according to reaction rates desired
369 c Change dimension of rsrc(i) if this is modified
370 c
371 c
372 c Compute the source rates of each species for which conservation eqn written
373 c Can be constant sources, zero sources (closed system), or chemical reaction
374 c
375 c Species numbering:
376 c 1 SO2(g) 6 S(IV)(aq)
377 c 2 O3(g) 7 O3(aq)
378 c 3 H2O2(g) 8 H2O2(aq)
379 c 4 NH3(g) 9 N(III)(aq)
380 c 5 HNO3(g) 10 N(V)(aq)
381 c
382 c
383 c source of S(VI) is reactions 1 and 2 in aqueous phase, due to O3 and H2O2
384 c
385 c hso3=ya(6)/(1+(h/ek(2))+(ek(3)/h))
386 c sol=ek(1)*hso3/h
387 c so2=ya(6)-hso3-so3
388 c
389 c r1=ya(7)*((2.4e4*so2)+(3.7e5*hso3)+1.5e9*so3)
390 c r2=7.45e7*h*ya(8)*hso3/(1+(13.*h))
391 c
392 c if no reactions are to be included, use following:
393 c
394 c r1=0.
395 c r2=0.
396 c
397 c following is gas source for open system:
398 c Note: unit conversion needed, aqueous is mol/l water; gas is mol/l air
399 c
400 c rsrc(1)=r1+r2*w1
401 c rsrc(2)=r1*w1
402 c rsrc(3)=r2*w1
403 c
404 c following is for closed system:
405 c
406 c rsrc(1)=0.
407 c rsrc(2)=0.
408 c rsrc(3)=0.
409 c
410 c r1=0.
411 c r2=0.
412 c

```

EX4A (cont'd)

```

* EXAMPLE 4:
* Initially at equilibrium
* Allow reaction to s(VI) to occur, but assume OPEN system
* Description of problem:
* Beginning with initial gas and aqueous concentrations of SO2, H2O2, NH3,
* HNO3, and O3, compute the conversion to s(VI)
* Set gas-phase sources equal to sinks in aqueous
* Species included and ordering:
* 1 SO2 g
* 2 O3 g
* 3 H2O2 g
* 4 NH3 g
* 5 HNO3 g
* 6 S(IV) = SO2 aq + HSO3- - SO3=
* 7 O3 aq
* 8 H2O2 aq
* 9 N(III) = NH4OH + NH4+
* 10 N(V) = HNO3 aq + NO3-
* 11 S(VI) = H2SO4 aq + HSO4- + SO4=
*
y 1 1.2e-10
y 2 2.045e-10
y 3 1.449e-11
y 4 7.101e-11
y 5 3.027e-19
y 6 8.446e-5
y 7 5.651e-11
y 8 2.641e-5
y 9 1.335e-4
y 10 4.09e-5
y 11 0.
temp 298.
wl 1.e-6
rad 10.e-4
xmfp .065e-4
diff 0.1
gauc 0.082058
xo 0.
ho .001
xstep 180.
iters 20
mf 22
etas 5.381e-01 5.381e-01 5.381e-01 5.381e-01 5.381e-01 5.381e-01 5.381e-01 5.381e-01 5.381e-01 5.381e-01 5.381e-01
kmt 1.614e-05 1.614e-05 1.614e-05 1.614e-05 1.614e-05 1.614e-05 1.614e-05 1.614e-05 1.614e-05 1.614e-05 1.614e-05
sk 1.230e-00 1.230e-02 6.610e-08 1.000e-03 1.020e-02 7.450e-04 2.100e-05 1.540e-01 1.130e-02 7.500e-01 1.750e-05 1.000e-14
time y1 y2 y3 y4 y5 y6 y7 y8 y9 y10 y11 pH

```

EX4B

```

0. 1.200e-10 2.045e-10 1.449e-11 7.101e-11 3.027e-19 8.446e-05 5.651e-11 2.641e-05 1.335e-04 4.090e-05 0. 6.233e-00
1.800e-02 1.803e-10 2.045e-10 1.501e-11 2.116e-11 1.392e-18 2.420e-05 5.643e-11 2.589e-05 1.833e-04 4.090e-05 5.550e-00
3.600e-02 2.005e-10 2.045e-10 1.506e-11 3.576e-12 9.086e-18 3.958e-06 5.651e-11 2.584e-05 2.009e-04 4.090e-05 5.750e-00
5.400e-02 2.033e-10 2.045e-10 1.507e-11 1.008e-12 3.255e-17 1.166e-06 5.651e-11 2.583e-05 2.035e-04 4.090e-05 5.814e-00
7.200e-02 2.038e-10 2.045e-10 1.507e-11 5.622e-13 5.845e-17 6.593e-07 5.651e-11 2.583e-05 2.039e-04 4.090e-05 5.840e-00
9.000e-02 2.040e-10 2.045e-10 1.507e-11 3.890e-13 8.455e-17 4.604e-07 5.651e-11 2.583e-05 2.041e-04 4.090e-05 5.850e-00
1.080e-03 2.041e-10 2.045e-10 1.507e-11 2.975e-13 1.106e-16 3.542e-07 5.651e-11 2.583e-05 2.042e-04 4.090e-05 5.850e-00
1.260e-03 2.042e-10 2.045e-10 1.507e-11 2.409e-13 1.366e-16 2.891e-07 5.651e-11 2.583e-05 2.043e-04 4.090e-05 5.850e-00
1.440e-03 2.042e-10 2.045e-10 1.507e-11 2.026e-13 1.625e-16 2.449e-07 5.651e-11 2.583e-05 2.043e-04 4.090e-05 5.850e-00
1.620e-03 2.042e-10 2.045e-10 1.507e-11 1.749e-13 1.883e-16 2.119e-07 5.651e-11 2.583e-05 2.043e-04 4.090e-05 5.850e-00
1.800e-03 2.043e-10 2.045e-10 1.507e-11 1.540e-13 2.139e-16 1.873e-07 5.651e-11 2.583e-05 2.044e-04 4.090e-05 5.850e-00
1.980e-03 2.043e-10 2.045e-10 1.507e-11 1.376e-13 2.394e-16 1.681e-07 5.651e-11 2.583e-05 2.044e-04 4.090e-05 5.850e-00
2.160e-03 2.043e-10 2.045e-10 1.507e-11 1.244e-13 2.648e-16 1.526e-07 5.651e-11 2.583e-05 2.044e-04 4.090e-05 5.850e-00
2.340e-03 2.043e-10 2.045e-10 1.507e-11 1.135e-13 2.901e-16 1.399e-07 5.651e-11 2.583e-05 2.044e-04 4.090e-05 5.850e-00
2.520e-03 2.043e-10 2.045e-10 1.507e-11 1.045e-13 3.153e-16 1.293e-07 5.651e-11 2.583e-05 2.044e-04 4.090e-05 5.850e-00
2.700e-03 2.043e-10 2.045e-10 1.507e-11 9.684e-14 3.403e-16 1.203e-07 5.651e-11 2.583e-05 2.044e-04 4.090e-05 5.850e-00
2.880e-03 2.043e-10 2.045e-10 1.507e-11 9.026e-14 3.653e-16 1.125e-07 5.651e-11 2.583e-05 2.044e-04 4.090e-05 5.850e-00
3.060e-03 2.044e-10 2.045e-10 1.507e-11 8.446e-14 3.901e-16 1.057e-07 5.651e-11 2.583e-05 2.044e-04 4.090e-05 5.850e-00
3.240e-03 2.044e-10 2.045e-10 1.507e-11 7.947e-14 4.148e-16 9.980e-08 5.651e-11 2.583e-05 2.044e-04 4.090e-05 5.850e-00
3.420e-03 2.044e-10 2.045e-10 1.507e-11 7.496e-14 4.395e-16 9.441e-08 5.651e-11 2.583e-05 2.044e-04 4.090e-05 5.850e-00
3.600e-03 2.044e-10 2.045e-10 1.507e-11 7.101e-14 4.640e-16 8.967e-08 5.651e-11 2.583e-05 2.044e-04 4.090e-05 5.850e-00
time ph h1 h2 h3 h4 h5 p1 p2 p3 p4 p5
0. 6.233e+00 2.881e+04 1.130e-02 7.450e+04 7.679e+04 5.533e+12 9.990e-01 1.000e+00 1.000e+00 1.001e+00 9.999e-01
1.800e+02 5.550e+00 5.490e+03 1.130e-02 7.450e+04 3.703e+05 1.146e+12 9.999e-01 9.986e-01 9.471e-01 9.567e-01 1.000e+00
3.600e+02 4.726e+00 8.097e+02 1.130e-02 7.450e+04 2.465e+06 1.722e+11 9.969e-01 1.000e+00 9.415e-01 9.323e-01 1.000e+00
5.400e+02 4.190e+00 2.356e+02 1.130e-02 7.450e+04 8.483e+06 5.004e+10 9.956e-01 1.000e+00 9.408e-01 9.730e-01 1.000e+00
7.200e+02 3.940e+00 1.332e+02 1.130e-02 7.450e+04 1.506e+07 2.818e+10 9.935e-01 1.000e+00 9.407e-01 9.850e-01 1.000e+00
9.000e+02 3.782e+00 9.283e+01 1.130e-02 7.450e+04 2.169e+07 1.957e+10 9.941e-01 1.000e+00 9.407e-01 9.895e-01 1.000e+00
1.080e+03 3.666e+00 7.141e+01 1.130e-02 7.450e+04 2.830e+07 1.500e+10 9.938e-01 1.000e+00 9.407e-01 9.920e-01 1.000e+00
1.260e+03 3.575e+00 5.814e+01 1.130e-02 7.450e+04 3.490e+07 1.216e+10 9.958e-01 1.000e+00 9.407e-01 9.935e-01 1.000e+00
1.440e+03 3.500e+00 4.913e+01 1.130e-02 7.450e+04 4.146e+07 1.024e+10 9.981e-01 1.000e+00 9.407e-01 9.968e-01 1.000e+00
1.620e+03 3.437e+00 4.260e+01 1.130e-02 7.450e+04 4.800e+07 8.843e+09 9.957e-01 1.000e+00 9.408e-01 9.953e-01 1.000e+00
1.800e+03 3.382e+00 3.766e+01 1.130e-02 7.450e+04 5.451e+07 7.787e+09 9.956e-01 1.000e+00 9.408e-01 9.958e-01 1.000e+00
1.980e+03 3.333e+00 3.379e+01 1.130e-02 7.450e+04 6.099e+07 6.960e+09 9.959e-01 1.000e+00 9.408e-01 9.962e-01 1.000e+00
2.160e+03 3.289e+00 3.068e+01 1.130e-02 7.450e+04 6.743e+07 6.295e+09 9.958e-01 1.000e+00 9.409e-01 9.965e-01 1.000e+00
2.340e+03 3.250e+00 2.812e+01 1.130e-02 7.450e+04 7.385e+07 5.748e+09 9.958e-01 1.000e+00 9.409e-01 9.968e-01 1.000e+00
2.520e+03 3.214e+00 2.598e+01 1.130e-02 7.450e+04 8.024e+07 5.290e+09 9.959e-01 1.000e+00 9.409e-01 9.969e-01 1.000e+00
2.700e+03 3.181e+00 2.416e+01 1.130e-02 7.450e+04 8.659e+07 4.902e+09 9.961e-01 1.000e+00 9.410e-01 9.969e-01 1.000e+00
2.880e+03 3.150e+00 2.260e+01 1.130e-02 7.450e+04 9.293e+07 4.568e+09 9.965e-01 1.000e+00 9.410e-01 9.966e-01 1.000e+00
3.060e+03 3.121e+00 2.124e+01 1.130e-02 7.450e+04 9.923e+07 4.278e+09 9.958e-01 1.000e+00 9.410e-01 9.974e-01 1.000e+00
3.240e+03 3.095e+00 2.005e+01 1.130e-02 7.450e+04 1.055e+08 4.024e+09 9.958e-01 1.000e+00 9.411e-01 9.971e-01 1.000e+00
3.420e+03 3.070e+00 1.900e+01 1.130e-02 7.450e+04 1.117e+08 3.799e+09 9.942e-01 1.000e+00 9.411e-01 9.981e-01 1.000e+00
3.600e+03 3.046e+00 1.806e+01 1.130e-02 7.450e+04 1.180e+08 3.598e+09 9.944e-01 1.000e+00 9.411e-01 9.980e-01 1.000e+00

```

5. Production of Sulfate in "Open" System Initially at Thermodynamic Equilibrium: Arbitrary Gas-Phase Source Rates

This simulation is similar to that of Example 4., but total production rate may differ from total consumption rate..

- (a) Run a Type 1 simulation (above) to find equilibrium gas and aqueous concentrations to use as initial conditions.
- (b) AQINP file: Initialize with equilibrium concentrations and set appropriate timesteps.
- (c) AQCHEM.FOR: Set rsrc(i) to compute depletion of S(IV), O₃, and H₂O₂ and to compute production of S(VI). Set rsrc(i) for the gas-phase species equal to the desired values (perhaps from a gas-phase chemistry simulation).
- (d) Compile and link.

Since this is essentially the same scheme as in Example 4., no numerical example is presented for this case.

6. Simulations of Systems Not Initially at Equilibrium

The same type of simulations described in Examples 2 - 5 above may be run without the assumption of initial equilibrium. Simply eliminate Step (a) in the procedure, and replace "equilibrium" in Step (b) with "desired".

Example: Reproduce example on pages 239-241 of Seinfeld (1986), except initial conditions are for total amounts of initial species in the gas phase only (all aqueous concentrations are zero). Assume a CLOSED system.

See AQINP file and RSOURCE used (Fig. EX6A), and output files (Fig. EX6B). Compare with Example 2.

In this Example, the drop must take up the gas-phase species at the same time as reactions are proceeding in the drop. Thus species which require a long time to equilibrate will impact the results differently from Example 2. We see that the difference between the two runs is negligible for the timesteps shown, consistent with the results of Example 1.

7. Simulations with Specified pH Held Constant

It may be desirable to assume the pH of the droplet is kept constant through some unspecified uptake processes, but the production and loss of other species are to be investigated as a function of this arbitrary pH. This assumption eliminates the need for the electroneutrality calculation. To set up a problem this way:

- (a) Set up as in Examples 1-6.
- (b) Change the subroutine ELECNEUT: Simply replace all statements after "include 'dropcl'" with a line stating, "h = (desired value)", making sure the lines "return" and "end" follow.
- (c) Compile and link.

Example: Compute production of S(VI) for a closed system held at pH=5.0, with other values as in Example 6.

See AQINP file and ELECNEUT used (Fig. EX7A), and output files (Fig. EX7B) and plot (Fig. EX7C). Compare with Example 6. In Example 6, the pH is greater than 5 for the time during which maximum S(VI) production rates occur. Since lowered pH inhibits the reaction with

```

* EXAMPLE 6:
* Allow reaction to s(VI) to occur, but assume CLOSED system
* Description of problem:
* Beginning with initial gas concentrations of SO2, H2O2, NH3,
* HNO3, and O3, compute the uptake of gas and conversion to s(VI)
* Set gas-phase sources equal to zero
* Species included and ordering:
  1 SO2 g
  2 O3 g
  3 H2O2 g
  4 NH3 g
  5 HNO3 g
  6 S(IV) = SO2 aq + H2O3 - + SO3=
  7 O3 aq
  8 H2O2 aq
  9 N(III) = NH4OH + NH4+
  10 N(V) = HNO3 aq + NO3-
  11 S(VI) = H2SO4 aq + HSO4- + SO4=
  Y 1 2.045e-10
  Y 2 2.045e-10
  Y 3 4.09e-11
  Y 4 2.045e-10
  Y 5 4.09e-11
  Y 6 0.
  Y 7 0.
  Y 8 0.
  Y 9 0.
  Y 10 0.
  Y 11 0.
  temp 298
  nl 1 e 6
  rad 10 e-4
  xatp .065e-4
  diff 0.1
  gasc 0.062058
  xc 0
  hco (m)
  xatp 18f
  iter 20

```

EX6A

```

360      subroutine rsource(ya,rsrc,h,t)
361 c
362 c Needs to have rate constants passed to it: also, for
363 c computing reaction rates, needs current conc's of reactants
364 c
365      dimension rsrc(11)
366      include 'dropcl'
367 c
368 c User supplies this subroutine according to reaction rates desired
369 c Change dimension of rsrc(i) if this is modified
370 c
371 c
372 c Compute the source rates of each species for which conservation eqm wri
tten
373 c Can be constant sources, zero sources (closed system), or chemical reac
tion
374 c
375 c Species numbering:
376 c   1 SO2(g)
377 c   2 O3(g)
378 c   3 H2O2(g)
379 c   4 NH3(g)
380 c   5 HNO3(g)
381 c
382 c
383 c source of S(VI) is reactions 1 and 2 in aqueous phase, due to O3 and H2
O2
384 c      hso3=ya(6)/(1.+h/ek(2))*(ek(3)/h)
385      snjek(1)=hso3/h
386      so2=ya(6)-hso3-so3
387
388 c      r1=ya(7)*((2.4e4*so2)*(3.7e5*hso3)*(1.5e9*so3))
389      r2=7.45e7*h*ya(8)*hso3/(1.+(13.*h))
390
391 c
392 c if no reactions are to be included, use following:
393 c
394 c      r1=0
395 c      r2=0
396 c
397 c following is gas source for open system:
398 c Note: unit conversion needed: aqueous is mol/l water; gas is mol/l air
399 c
400 c      rsrc(1)=(r1+r2)*w1
401 c      rsrc(2)=r1*w1
402 c      rsrc(3)=r2*w1
403 c
404 c Following is for closed system:
405 c
406 c      rsrc(1)=0.
407 c      rsrc(2)=0.
408 c      rsrc(3)=0.
409 c
410 c      rsrc(4)=0.
411 c      rsrc(5)=0.
412 c

```

```

Session Name: 128.55.128.130.4
413      rsrc(6)=r1-r2
414      rsrc(7)=r1
415      rsrc(8)=r2
416      rsrc(9)=0.
417      rsrc(10)=0.
418 c
419      rsrc(11)=r1+r2
420 c
421      return
422      end

```

```

* EXAMPLE 6:
* Allow reaction to s(VI) to occur, but assume CLOSED system
* Description of problem:
* Beginning with initial gas concentrations of SO2, H2O2, NH3,
* HNO3, and O3, compute the uptake of gas and conversion to s(VI)
* Set gas-phase sources equal to zero
* Species included and ordering:
* 1 SO2 g
* 2 O3 g
* 3 H2O2 g
* 4 NH3 g
* 5 HNO3 g
* 6 S(IV) = SO2 aq + HSO3- + SO3=
* 7 O3 aq
* 8 H2O2 aq
* 9 N(III) = NH4OH + NH4+
* 10 N(V) = HNO3 aq + NO3-
* 11 S(VI) = H2SO4 aq + HSO4- + SO4=
*
y 1 2.045e-10
y 2 2.045e-10
y 3 4.09e-11
y 4 2.045e-10
y 5 4.09e-11
y 6 0.
y 7 0.
y 8 0.
y 9 0.
y 10 0.
y 11 0.
temp 298.
wl 1.e-6
rad 10.e-4
xmfp .065e-4
diff 0.1
gasc 0.082058
xo 0.
ho .001
xstep 180.
iters 20
mf 22
eras 5.381e-01 5.381e-01 5.381e-01 5.381e-01 5.381e-01 5.381e-01 5.381e-01 5.381e-01 5.381e-01 5.381e-01 5.381e-01 5.381e-01
kmc 1.614e-05 1.614e-05 1.614e-05 1.614e-05 1.614e-05 1.614e-05 1.614e-05 1.614e-05 1.614e-05 1.614e-05 1.614e-05 1.614e-05
ek 1.230e-00 1.230e-02 6.610e-08 1.000e-03 1.020e-02 7.450e-04 2.100e-05 1.540e-01 1.130e-02 7.500e-01 1.750e-05 1.000e-14
time y1 y2 y3 y4 y5 y6 y7 y8 y9 y10 y11 pH
0. 2.045e-10 2.045e-10 4.090e-11 2.045e-10 4.090e-11 0. 0. 0. 0. 0. 0. 7.011e-01

```

EX6B

```

1.800e-02 1.244e-10 1.646e-10 9.957e-12 3.131e-11 1.506e-18 2.708e-05 4.536e-11 1.789e-05 1.732e-04 4.090e-05 5.299e-05 5.754e-11
3.600e-02 1.230e-10 1.583e-10 6.712e-12 1.701e-11 1.774e-18 1.323e-05 4.372e-11 1.206e-05 1.875e-04 4.090e-05 6.832e-05 5.456e-11
5.400e-02 1.210e-10 1.566e-10 4.550e-12 1.009e-11 3.101e-18 7.418e-06 4.326e-11 8.179e-06 1.944e-04 4.090e-05 7.608e-05 5.215e-11
7.200e-02 1.190e-10 1.560e-10 3.104e-12 6.703e-12 4.754e-18 4.765e-06 4.309e-11 5.581e-06 1.978e-04 4.090e-05 8.075e-05 5.031e-11
9.000e-02 1.172e-10 1.557e-10 2.131e-12 5.051e-12 6.362e-18 3.516e-06 4.301e-11 3.832e-06 1.994e-04 4.090e-05 8.377e-05 4.907e-11
1.080e-03 1.158e-10 1.555e-10 1.470e-12 4.196e-12 7.692e-18 2.881e-06 4.296e-11 2.644e-06 2.003e-04 4.090e-05 8.581e-05 4.825e-11
1.260e-03 1.148e-10 1.553e-10 1.018e-12 3.715e-12 8.707e-18 2.527e-06 4.292e-11 1.831e-06 2.008e-04 4.090e-05 8.721e-05 4.777e-11
1.440e-03 1.140e-10 1.552e-10 7.069e-13 3.425e-12 9.461e-18 2.312e-06 4.289e-11 1.272e-06 2.011e-04 4.090e-05 8.819e-05 4.731e-11
1.620e-03 1.134e-10 1.551e-10 4.920e-13 3.239e-12 1.001e-17 2.174e-06 4.287e-11 8.851e-07 2.013e-04 4.090e-05 8.889e-05 4.711e-11
1.800e-03 1.130e-10 1.550e-10 3.429e-13 3.113e-12 1.043e-17 2.082e-06 4.284e-11 6.170e-07 2.014e-04 4.090e-05 8.939e-05 4.695e-11
1.980e-03 1.127e-10 1.550e-10 2.393e-13 3.026e-12 1.073e-17 2.018e-06 4.282e-11 4.305e-07 2.015e-04 4.090e-05 8.976e-05 4.683e-11
2.160e-03 1.125e-10 1.549e-10 1.671e-13 2.962e-12 1.096e-17 1.971e-06 4.280e-11 3.006e-07 2.015e-04 4.090e-05 9.004e-05 4.673e-11
2.340e-03 1.123e-10 1.548e-10 1.167e-13 2.915e-12 1.114e-17 1.937e-06 4.278e-11 2.100e-07 2.016e-04 4.090e-05 9.026e-05 4.666e-11
2.520e-03 1.122e-10 1.547e-10 8.158e-14 2.879e-12 1.129e-17 1.910e-06 4.276e-11 1.468e-07 2.016e-04 4.090e-05 9.043e-05 4.661e-11
2.700e-03 1.120e-10 1.547e-10 5.704e-14 2.849e-12 1.140e-17 1.888e-06 4.274e-11 1.026e-07 2.017e-04 4.090e-05 9.057e-05 4.656e-11
2.880e-03 1.119e-10 1.546e-10 3.990e-14 2.825e-12 1.150e-17 1.870e-06 4.272e-11 7.179e-08 2.017e-04 4.090e-05 9.069e-05 4.652e-11
3.060e-03 1.119e-10 1.545e-10 2.792e-14 2.804e-12 1.159e-17 1.855e-06 4.270e-11 5.024e-08 2.017e-04 4.090e-05 9.079e-05 4.649e-11
3.240e-03 1.118e-10 1.545e-10 1.955e-14 2.786e-12 1.167e-17 1.841e-06 4.268e-11 3.518e-08 2.017e-04 4.090e-05 9.088e-05 4.647e-11
3.420e-03 1.117e-10 1.544e-10 1.370e-14 2.769e-12 1.174e-17 1.829e-06 4.266e-11 2.465e-08 2.017e-04 4.090e-05 9.097e-05 4.644e-11
3.600e-03 1.116e-10 1.543e-10 9.591e-15 2.754e-12 1.180e-17 1.818e-06 4.264e-11 1.726e-08 2.017e-04 4.090e-05 9.104e-05 4.642e-11
time ph h1 h2 h3 h4 h5 p1 p2 p3 p4 p5
0. 7.000e+00 2.513e-05 1.130e-02 7.450e-04 1.320e-04 3.234e+13 0. 0. 0. 0. 0.
1.800e-02 5.754e+00 8.901e-03 1.130e-02 7.450e-04 2.315e-05 1.834e+12 9.997e-01 9.975e-01 9.864e-01 9.770e-01 6.058e-01
3.600e-02 5.456e+00 4.404e-03 1.130e-02 7.450e-04 4.596e-05 9.236e+11 9.995e-01 9.994e-01 9.865e-01 9.807e-01 1.021e+00
5.400e-02 5.215e+00 2.509e-03 1.130e-02 7.450e-04 8.006e-05 5.102e+11 9.994e-01 9.998e-01 9.867e-01 9.838e-01 1.017e+00
7.200e-02 5.031e+00 1.639e-03 1.130e-02 7.450e-04 1.221e-06 3.476e+11 9.994e-01 9.999e-01 9.869e-01 9.882e-01 1.012e+00
9.000e-02 4.907e+00 1.228e-03 1.130e-02 7.450e-04 1.628e-06 2.608e+11 9.993e-01 9.999e-01 9.872e-01 9.920e-01 1.008e+00
1.080e-03 4.825e+00 1.018e-03 1.130e-02 7.450e-04 1.962e-06 2.163e+11 9.996e-01 1.000e+00 9.873e-01 9.948e-01 1.005e+00
1.260e-03 4.772e+00 9.003e-02 1.130e-02 7.450e-04 2.217e-06 1.914e+11 1.000e+00 1.000e+00 9.874e-01 9.967e-01 1.003e+00
1.440e-03 4.737e+00 8.293e-02 1.130e-02 7.450e-04 2.407e-06 1.764e+11 9.998e-01 1.000e+00 9.875e-01 9.977e-01 1.002e+00
1.620e-03 4.712e+00 7.839e-02 1.130e-02 7.450e-04 2.546e-06 1.667e+11 9.997e-01 1.000e+00 9.876e-01 9.983e-01 1.002e+00
1.800e-03 4.695e+00 7.534e-02 1.130e-02 7.450e-04 2.649e-06 1.603e+11 1.000e+00 1.000e+00 9.876e-01 9.989e-01 1.001e+00
1.980e-03 4.683e+00 7.321e-02 1.130e-02 7.450e-04 2.725e-06 1.557e+11 9.999e-01 1.000e+00 9.876e-01 9.991e-01 1.001e+00
2.160e-03 4.673e+00 7.167e-02 1.130e-02 7.450e-04 2.784e-06 1.525e+11 1.000e+00 1.000e+00 9.877e-01 9.993e-01 1.001e+00
2.340e-03 4.666e+00 7.052e-02 1.130e-02 7.450e-04 2.829e-06 1.500e+11 1.000e+00 1.000e+00 9.876e-01 9.997e-01 1.001e+00
2.520e-03 4.661e+00 6.963e-02 1.130e-02 7.450e-04 2.865e-06 1.481e+11 9.999e-01 1.000e+00 9.877e-01 9.995e-01 1.000e+00
2.700e-03 4.656e+00 6.891e-02 1.130e-02 7.450e-04 2.895e-06 1.466e+11 1.000e+00 1.000e+00 9.877e-01 9.996e-01 1.000e+00
2.880e-03 4.653e+00 6.832e-02 1.130e-02 7.450e-04 2.920e-06 1.454e+11 9.999e-01 1.000e+00 9.877e-01 9.998e-01 1.000e+00
3.060e-03 4.649e+00 6.782e-02 1.130e-02 7.450e-04 2.942e-06 1.443e+11 9.999e-01 1.000e+00 9.878e-01 9.998e-01 1.000e+00
3.240e-03 4.647e+00 6.737e-02 1.130e-02 7.450e-04 2.961e-06 1.433e+11 9.999e-01 1.000e+00 9.877e-01 9.998e-01 1.000e+00
3.420e-03 4.644e+00 6.697e-02 1.130e-02 7.450e-04 2.979e-06 1.425e+11 1.000e+00 1.000e+00 9.877e-01 9.998e-01 1.000e+00
3.600e-03 4.642e+00 6.659e-02 1.130e-02 7.450e-04 2.996e-06 1.417e+11 9.999e-01 1.000e+00 9.880e-01 9.997e-01 1.000e+00

```



```

* EXAMPLE 7:
* Allow reaction to s(VI) to occur, but assume CLOSED system
* Set pH=constant=5
* Description of problem:
* Beginning with initial gas concentrations of SO2, H2O2, NH3,
* HNO3, and O2, compute the uptake of gas and conversion to s(VI)
* Set gas-phase sources equal to zero
* Modify subroutine ELECNEUT
* Species included and ordering:
* 1 SO2 g
* 2 O2 g
* 3 H2O2 g
* 4 NH3 g
* 5 HNO3 g
* 6 S(IV) = SO2 aq + HSO3- + SO3=
* 7 O3 aq
* 8 H2O2 aq
* 9 N(III) = NH4OH + NH4+
* 10 N(V) = HNO3 aq + NO3-
* 11 S(VI) = H2SO4 aq + HSO4- + SO4=
*
y 1 2.045e-10
y 2 2.045e-10
y 3 4.09e-11
y 4 2.045e-10
y 5 4.09e-11
y 6 0.
y 7 0.
y 8 0.
y 9 0.
y 10 0.
y 11 0.
temp 298.
wt 1.e-6
rad 10.e-4
xmfp .065e-4
diff 0.1
gasc 0.082058
xo 0.
ho .001
xstep 180.
iters 20
mf 22
etas 5.381e-01 5.381e-01 5.381e-01 5.381e-01 5.381e-01 5.381e-01 5.381e-01 5.381e-01 5.381e-01 5.381e-01 5.381e-01 5.381e-01
knt 1.614e-05 1.614e-05 1.614e-05 1.614e-05 1.614e-05 1.614e-05 1.614e-05 1.614e-05 1.614e-05 1.614e-05 1.614e-05 1.614e-05
ek 1.230e-00 1.230e-02 6.610e-08 1.000e+03 1.020e-02 7.450e-04 2.100e+05 1.540e+01 1.130e-02 7.500e-01 1.750e-05 1.300e-14

```

EX7B

time	y1	y2	y3	y4	y5	y6	y7	y8	y9	y10	y11	pH
0.	2.045e-10	2.045e-10	4.090e-11	2.045e-10	4.090e-11	0.	0.	0.	0.	0.	0.	5.000e-00
1.800e-02	1.791e-10	2.038e-10	8.221e-12	6.179e-12	5.182e-10	6.659e-06	5.630e-11	1.468e-05	1.983e-04	4.090e-05	1.872e-05	5.000e-00
3.600e-02	1.691e-10	2.031e-10	4.734e-12	6.179e-12	5.145e-10	6.293e-06	5.612e-11	8.464e-06	1.983e-04	4.090e-05	2.909e-05	5.000e-00
5.400e-02	1.613e-10	2.025e-10	2.792e-12	6.179e-12	5.179e-10	6.080e-06	5.594e-11	4.996e-06	1.983e-04	4.090e-05	3.514e-05	5.000e-00
7.200e-02	1.597e-10	2.019e-10	1.671e-12	6.179e-12	5.182e-10	5.947e-06	5.577e-11	2.992e-06	1.983e-04	4.090e-05	3.888e-05	5.000e-00
9.000e-02	1.573e-10	2.013e-10	1.010e-12	6.179e-12	5.183e-10	5.861e-06	5.561e-11	1.808e-06	1.983e-04	4.090e-05	4.133e-05	5.000e-00
1.080e-01	1.557e-10	2.007e-10	6.138e-13	6.179e-12	5.215e-10	5.800e-06	5.544e-11	1.099e-06	1.983e-04	4.090e-05	4.303e-05	5.000e-00
1.260e-01	1.545e-10	2.001e-10	3.748e-13	6.179e-12	5.157e-10	5.755e-06	5.528e-11	6.712e-07	1.983e-04	4.090e-05	4.428e-05	5.000e-00
1.440e-01	1.535e-10	1.995e-10	2.296e-13	6.179e-12	5.136e-10	5.720e-06	5.512e-11	4.113e-07	1.983e-04	4.090e-05	4.527e-05	5.000e-00
1.620e-01	1.527e-10	1.989e-10	1.411e-13	6.179e-12	5.194e-10	5.691e-06	5.496e-11	2.527e-07	1.983e-04	4.090e-05	4.609e-05	5.000e-00
1.800e-01	1.520e-10	1.983e-10	8.688e-14	6.179e-12	5.167e-10	5.665e-06	5.480e-11	1.556e-07	1.983e-04	4.090e-05	4.682e-05	5.000e-00
1.980e-01	1.514e-10	1.978e-10	5.264e-14	6.179e-12	5.173e-10	5.641e-06	5.464e-11	9.610e-08	1.983e-04	4.090e-05	4.748e-05	5.000e-00
2.160e-01	1.508e-10	1.972e-10	3.318e-14	6.179e-12	5.219e-10	5.619e-06	5.449e-11	5.947e-08	1.983e-04	4.090e-05	4.810e-05	5.000e-00
2.340e-01	1.502e-10	1.966e-10	2.058e-14	6.179e-12	5.167e-10	5.598e-06	5.433e-11	3.687e-08	1.983e-04	4.090e-05	4.869e-05	5.000e-00
2.520e-01	1.496e-10	1.961e-10	1.280e-14	6.179e-12	5.162e-10	5.577e-06	5.418e-11	2.293e-08	1.983e-04	4.090e-05	4.927e-05	5.000e-00
2.700e-01	1.491e-10	1.955e-10	7.971e-15	6.179e-12	5.205e-10	5.556e-06	5.403e-11	1.430e-08	1.983e-04	4.090e-05	4.984e-05	5.000e-00
2.880e-01	1.486e-10	1.950e-10	4.978e-15	6.179e-12	5.210e-10	5.536e-06	5.387e-11	8.944e-09	1.983e-04	4.090e-05	5.040e-05	5.000e-00
3.060e-01	1.480e-10	1.944e-10	3.130e-15	6.179e-12	5.166e-10	5.516e-06	5.372e-11	5.592e-09	1.983e-04	4.090e-05	5.095e-05	5.000e-00
3.240e-01	1.475e-10	1.939e-10	1.960e-15	6.179e-12	5.174e-10	5.497e-06	5.357e-11	3.520e-09	1.983e-04	4.090e-05	5.150e-05	5.000e-00
3.420e-01	1.470e-10	1.934e-10	1.237e-15	6.179e-12	5.177e-10	5.477e-06	5.342e-11	2.221e-09	1.983e-04	4.090e-05	5.204e-05	5.000e-00
3.600e-01	1.465e-10	1.928e-10	7.876e-16	6.179e-12	5.171e-10	5.458e-06	5.328e-11	1.409e-09	1.983e-04	4.090e-05	5.258e-05	5.000e-00

time	ph	h1	h2	h3	h4	h5	p1	p2	p3	p4	p5
0.	5.000e+00	1.524e+03	1.130e-02	7.450e+04	1.313e+06	3.234e+11	0.	0.	0.	0.	0.
1.800e-02	5.000e+00	1.524e+03	1.130e-02	7.450e+04	1.313e+06	3.234e+11	9.975e-01	9.999e-01	9.804e-01	1.000e+00	9.980e-01
3.600e-02	5.000e+00	1.524e+03	1.130e-02	7.450e+04	1.313e+06	3.234e+11	9.985e-01	9.999e-01	9.815e-01	1.000e+00	1.005e+00
5.400e-02	5.000e+00	1.524e+03	1.130e-02	7.450e+04	1.313e+06	3.234e+11	9.991e-01	9.999e-01	9.821e-01	1.000e+00	9.985e-01
7.200e-02	5.000e+00	1.524e+03	1.130e-02	7.450e+04	1.313e+06	3.234e+11	9.994e-01	9.999e-01	9.825e-01	1.000e+00	9.980e-01
9.000e-02	5.000e+00	1.524e+03	1.130e-02	7.450e+04	1.313e+06	3.234e+11	9.996e-01	9.999e-01	9.828e-01	1.000e+00	9.979e-01
1.080e-01	5.000e+00	1.524e+03	1.130e-02	7.450e+04	1.313e+06	3.234e+11	9.997e-01	9.999e-01	9.829e-01	1.000e+00	9.918e-01
1.260e-01	5.000e+00	1.524e+03	1.130e-02	7.450e+04	1.313e+06	3.234e+11	9.998e-01	9.999e-01	9.831e-01	1.000e+00	1.003e+00
1.440e-01	5.000e+00	1.524e+03	1.130e-02	7.450e+04	1.313e+06	3.234e+11	9.998e-01	9.999e-01	9.832e-01	1.000e+00	1.007e+00
1.620e-01	5.000e+00	1.524e+03	1.130e-02	7.450e+04	1.313e+06	3.234e+11	9.998e-01	9.999e-01	9.833e-01	1.000e+00	9.957e-01
1.800e-01	5.000e+00	1.524e+03	1.130e-02	7.450e+04	1.313e+06	3.234e+11	9.998e-01	9.999e-01	9.834e-01	1.000e+00	9.936e-01
1.980e-01	5.000e+00	1.524e+03	1.130e-02	7.450e+04	1.313e+06	3.234e+11	9.999e-01	9.999e-01	9.834e-01	1.000e+00	9.936e-01
2.160e-01	5.000e+00	1.524e+03	1.130e-02	7.450e+04	1.313e+06	3.234e+11	9.999e-01	9.999e-01	9.834e-01	1.000e+00	9.910e-01
2.340e-01	5.000e+00	1.524e+03	1.130e-02	7.450e+04	1.313e+06	3.234e+11	9.999e-01	9.999e-01	9.834e-01	1.000e+00	1.001e+00
2.520e-01	5.000e+00	1.524e+03	1.130e-02	7.450e+04	1.313e+06	3.234e+11	9.999e-01	9.999e-01	9.835e-01	1.000e+00	1.002e+00
2.700e-01	5.000e+00	1.524e+03	1.130e-02	7.450e+04	1.313e+06	3.234e+11	9.999e-01	9.999e-01	9.848e-01	1.000e+00	9.936e-01
2.880e-01	5.000e+00	1.524e+03	1.130e-02	7.450e+04	1.313e+06	3.234e+11	9.999e-01	9.999e-01	9.862e-01	1.000e+00	9.926e-01
3.060e-01	5.000e+00	1.524e+03	1.130e-02	7.450e+04	1.313e+06	3.234e+11	9.999e-01	9.999e-01	9.807e-01	1.000e+00	1.001e+00
3.240e-01	5.000e+00	1.524e+03	1.130e-02	7.450e+04	1.313e+06	3.234e+11	9.999e-01	9.999e-01	9.859e-01	1.000e+00	9.996e-01
3.420e-01	5.000e+00	1.524e+03	1.130e-02	7.450e+04	1.313e+06	3.234e+11	9.999e-01	9.999e-01	9.854e-01	1.000e+00	9.990e-01
3.600e-01	5.000e+00	1.524e+03	1.130e-02	7.450e+04	1.313e+06	3.234e+11	9.999e-01	9.999e-01	9.817e-01	1.000e+00	1.000e-01

ozone, we would expect less S(VI) formation if the pH is set to 5. From Fig. EX7C, we note the S(VI) produced is less than 60% of that produced in Examples 6 and 2. Also, as expected, the initial production rates in Example 7 are not as fast as those in Example 6.

Comment

These various modes discussed in Examples 1 through 7 all require that the code be recompiled and linked. Separate executables with different names could be made for each type of case, if it is to be studied more than once. For example, edit LODAQ so that $x=xphconst$ for a code that holds pH constant as in Example 7. This code can then be used to investigate what effects changing the inputs available through AQINP have upon the results (for example, response to temperature changes).

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Appendix A:
Derivation of equations for electroneutrality condition

Electroneutrality Equations

①

POS: H^+ , NH_4^+

NEG: OH^- , HSO_3^- , $2 SO_3^{2-}$, $2 SO_4^{2-}$, HSO_4^- , NO_3^-

Put all species in terms of $[H^+]$ + K_{eq} , "nonionic" (yes)

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{K_{12}}{[H^+]}$$

$$\begin{aligned} N(III) &= NH_4OH + NH_4^+ = \frac{[NH_4^+][OH^-]}{K_{11}} + [NH_4^+] \\ &= \frac{[NH_4^+]}{K_{11}} \frac{K_{12}}{[H^+]} + [NH_4^+] \\ &= [NH_4^+] \left\{ 1 + \frac{K_{12}}{K_{11}} \frac{1}{[H^+]} \right\} \end{aligned}$$

$$\begin{aligned} N(V) &= HNO_3 \cdot aq + NO_3^- \\ &= \frac{[NO_3^-][H^+]}{K_8} + [NO_3^-] = [NO_3^-] \left\{ 1 + \frac{[H^+]}{K_8} \right\} \end{aligned}$$

Thus

$$[NH_4^+] = N(III) / \left[1 + \frac{K_{12}}{K_{11}} \frac{1}{[H^+]} \right]$$

$$[NO_3^-] = N(V) / \left[1 + [H^+] / K_8 \right]$$

For sulfur species

ELEMENT is passed total $S(IV)$, $S(VI)$ + $[H^+]$.

$$H_2SO_4 \text{ aq} = \frac{[HSO_4^-][H^+]}{K_4} = \underbrace{S(VI) - HSO_4^- - SO_4^{2-}}_{\text{mass balance}}$$

(2)

$$\text{So, } \frac{S(VI)}{[HSO_4^-]} - 1 - \frac{[SO_4^{2-}]}{[HSO_4^-]} = \frac{[H^+]}{K_4}$$

↙ equals $\frac{K_5}{[H^+]}$

Rearranging

$$[HSO_4^-] = S(VI) / \left(1 + \frac{K_5}{[H^+]} + \frac{[H^+]}{K_4} \right)$$

and it follows

$$[SO_4^{2-}] = \frac{K_5 [HSO_4^-]}{[H^+]} \quad (\text{compute } [HSO_4^-] \text{ first})$$

Similarly for S(IV):

$$[SO_2 \cdot H_2O] = \frac{[HSO_3^-][H^+]}{K_2} = S(IV) - HSO_3^- - \underbrace{SO_3^{2-}}_{\substack{\downarrow \\ \frac{K_3 [HSO_3^-]}{[H^+]}}}$$

Rearrange,

$$[HSO_3^-] = S(IV) / \left\{ 1 + \frac{[H^+]}{K_2} + \frac{K_3}{[H^+]} \right\}$$

Then it follows

$$[SO_3^{2-}] = \frac{K_3 [HSO_3^-]}{[H^+]}$$

Derivatives with respect to $[H^+]$

(3)

$$d(\text{POS}) \Rightarrow \frac{d[H^+]}{d[H^+]} = 1$$

$$\frac{d[NH_4^+]}{d[H^+]} = \frac{-N(\text{III})}{\left(1 + \frac{K_{12}}{K_{11}} \frac{1}{[H^+]}\right)^2} \left(-\frac{K_{12}}{K_{11}}\right) \frac{1}{[H^+]^2}$$

$d(\text{NEG}) \Rightarrow$

$$\frac{d[OH^-]}{d[H^+]} = -K_{12} / [H^+]^2$$

$$\frac{d[NO_3^-]}{d[H^+]} = \frac{-N(V)}{\left(1 + \frac{[H^+]}{K_8}\right)^2} \frac{1}{K_8}$$

$$\frac{d[HSO_4^-]}{d[H^+]} = \frac{-S(VI)}{\left(1 + \frac{K_5}{H} + \frac{H}{K_4}\right)^2} \left(-\frac{K_5}{H^2} + \frac{1}{K_4}\right)$$

$$\frac{d[SO_4^{2-}]}{d[H^+]} = \frac{K_5}{[H^+]} \frac{d[HSO_4^-]}{d[H^+]} + [HSO_4^-] K_5 \left(-\frac{1}{H^2}\right)$$

$$\frac{d[HSO_3^-]}{d[H^+]} = \frac{-S(IV)}{\left(1 + \frac{H}{K_2} + \frac{K_3}{H}\right)^2} \left[\frac{1}{K_2} - \frac{K_3}{H^2}\right]$$

$$\frac{d[SO_3^{2-}]}{d[H^+]} = \frac{K_3}{H^+} \frac{d[HSO_3^-]}{d[H^+]} + [HSO_3^-] \left(\frac{-K_3}{H^2}\right)$$

Appendix B: Overview of sulfate-production mechanisms and importance

Summary:

The uptake of sulfur dioxide (SO_2) by cloud droplets and the aqueous chemical conversion of S(IV) species to S(VI) species was studied using a simple model of these processes. The distribution of sulfur ions as a function of pH was modeled, and it was shown that the dominant S(IV) $\rightarrow$ S(VI) chemical conversion pathway in aqueous solution is highly dependent upon pH, with the reaction $\text{S(IV)} + \text{H}_2\text{O}_2 \rightarrow \text{S(VI)}$ being the most important source of sulfate at pH levels normally found in natural cloudwaters. The effects of other dissolved species (such as nitrogen species and metal catalysts) were investigated through a literature survey.

Report:

The dissolution of SO_2 into the aqueous phase is governed by the effective Henry's Law constant, $H^*\text{S(IV)}$, which is related to the conventional Henry's Law coefficient H_{SO_2} . The effective coefficient takes into account the dissociation of aqueous SO_2 into its various S(IV) aqueous species, that the total amount of dissolved sulfur exceeds that predicted by Henry's Law for SO_2 alone, and the total amount of dissolved S(IV) is highly pH-dependent. The equilibrium dissolved S(IV) also depends upon temperature, with lower temperatures favoring higher aqueous concentrations.

A number of reactions converting S(IV) to S(VI) may occur in the liquid phase. S(IV) may be oxidized by reaction with dissolved ozone, dissolved hydrogen peroxide, and dissolved oxygen, although the reaction with oxygen is unimportant unless catalyzed by another species, such as iron, manganese, or carbon. The reaction with dissolved H_2O_2 is an order of magnitude more important than any other reaction rate up to a pH of 5; at higher pH, the ozone reactions become important. Measured cloudwater pH is in the range 3 - 6; rain, 4 - 5; and fog, 2 - 6. (The pH of some hazes may be as low as 1, but these are not considered here.) Based upon these typical pH ranges, we selected as the focus of the present study the reaction of sulfur species with $\text{H}_2\text{O}_2(\text{aq})$ and $\text{O}_3(\text{aq})$.

In studying the chemical reaction rates for species dissolved in cloud droplets, the system may be modeled as either *open* or *closed*. In a closed system, the total quantity of each species is fixed. Thus, fixed amounts of SO_2 and oxidizing species are dissolved in a droplet at time zero, and the reactions proceed until either equilibrium or until consumption of the limiting reagent. Such a scheme would represent a droplet that occupies the same space as the surrounding gas and the gaseous species are not replenished. If the cloud droplet has air continuously passing over it -- i.e., the cloud is "processing" air parcels -- then the concept of an open system would be more appropriate. In this case, the partial pressures of the gas-phase species are maintained at some constant value, representing a reservoir from which the droplet can continuously draw. These two cases represent limiting conditions, with a true cloud droplet experiencing conditions intermediate to these two.

Previous work (Seinfeld, 1987) has shown that the closed system reaches a lower pH, and does so much more quickly than the open system, if neutralization by dissolved ammonia (NH_3) is included in the model. This is because the open system can continue to draw NH_3 from the environment to keep the pH from decreasing too rapidly, effectively shutting off the oxidation reactions.

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