Modelling Stratospheric Ozone Kinetics, Part II ©

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Prerequisites: This worksheet is appropriate for use in Junior-Senior level physical chemistry classes**.** To use the document you should have completed the companion document "Modelling Stratospheric Ozone Kinetics, Part I." This document requires Mathcad 6.0+ (professional version) or later.

Goal: This pair of documents, Modeling Stratospheric Ozone Kinetics Part I and Part II, is designed to lead students into modelling the kinetics of stratospheric ozone reactions. Part I focuses on the mechanics of the modelling method and considers only the Chapman cycle of reactions for stratospheric ozone. In Part II, students incorporate a larger set of reactions including the HO_x, NO_x and ClO_x reaction cycles.

Performance Objectives: After completing the work described in this document you should be able to:

1. use Mathcad to set up and numerically solve systems of differential equations to explore the time evolution of a chemical system
2. add reactions and complexity to the model
3. recognize and discuss the tradeoffs that face modellers of chemical kinetics
4. discuss the relative importance of the ClO_x, NO_x and HO_x cycles to stratospheric ozone chemistry

Introduction: Stratospheric ozone kinetics remains an active area of research for atmospheric chemists. The basic reaction cycles are well established and a regularly-updated comprehensive treatment of kinetic data is available (Chemical Kinetics and Photochemical Data for Use in Stratospheric Modelling, Evaluation Number 12, Jet Propulsion Laboratory: Pasadena, 1997 (JPL Publication 97-4, available electronically at http://remus.jpl.nasa.gov/jpl97/)).

Several naturally-occurring atmospheric constituents react with the oxygen-containing species considered in Part I of this document. Major players among these are the NO_x and HO_x molecules (NO, NO_2, HO, HO_2). Addition of the chemical reactions involving these species helps make our model a more realistic description of stratospheric chemistry. Specific variables that can be explored for the stratospheric ozone reactions in this document include temperature, pressure, initial component concentrations and the number of reactions and components to be considered.

The document is structured so that the reader is first asked in a series of leading exercises to set up and solve the system of differential equations involving the NO_x and HO_x cycles, then to investigate the effects of changes in the input values. All of the answers to the "set-up" section are given at the end of the document, which means that readers wishing to investigate chemical questions and avoid modelling details can skip the set-up exercises and use the ready-made template in the answers section at the end of the worksheet. In this way, the document can either function as a bridge toward independent set-up of more complex models or as a stand-alone modelling template with emphasis on chemical questions about the system and the model. The necessary data are provided for addition of the ClO_x reactions, but actual incorporation of these reactions into the model is left as a mastery exercise.

Unless otherwise noted, reported rate constants, initial concentrations and total number density of atmospheric constituents are the values associated with an altitude of 25 km and a temperature of 220 K; all numerical values were taken to the best of the authors' ability from Tables 1 and 2 and Appendix III of the JPL document cited in the first paragraph of this Introduction.

Helpful hints:

As you read through Section 1, you will notice a number of undefined variables and error messages. Don't panic! As you work the exercises, you will define the variables and the error messages should disappear. (In the answers section, all variables are defined and no error messages appear.)

If Mathcad starts to show a lightbulb cursor, it is performing one of the calculations embedded in this document. Press the escape key to interrupt the processing. Start processing again by choosing "Calculate worksheet" from the Math menu. Alternatively, turn off the checkmark beside Automatic mode in the Math menu. When automatic mode is de-selected, you must push the F9 key to start EVERY calculation, even seemingly trivial ones. Calculation times of one to two minutes are typical for calculations in this worksheet with Mathcad installed on a 120 MHz Pentium.

To make additional space in the document, add blank lines by using control-F9 in Mathcad 6.0 or the enter key in later versions. Lines can be deleted from the document with the keystroke control-F10.

Units are shown in the text, but are not generally used in the calculations because the differential equation solver requires unitless inputs.

Section 1. Setting up and solving the model

In the previous document, Modelling Stratospheric Ozone Kinetics, Part I, we considered the kinetics of the reactions making up the Chapman cycle (oxygen species only, Steps 1-4 in the mechanism below.) In this Part II document, the reader is led through the addition of the naturally-occurring NO_x and HO_x ozone-destruction cycles (Steps 5-8 in the mechanism below) to the previously-considered Chapman reactions.

Photolysis rate constants are reported directly to the right of the chemical equations in Steps 1 and 3, below. As described in the Part I document, second- and third-order rate constants can be calculated from the parameters provided to the right of the chemical equations in Steps 2 and 4-8. Formulas for the temperature-dependence of second- and third-order rate constants are given after Exercise 1.

Step 1	O_2 + hν ---> 2 O	k_1 = 3 x 10^{-12} sec^{-1}
Step 2	M + O + O_2 ---> M + O_3	ko_2 = 6.0 x 10^{-34}; n_2 = 2.3
Step 3	O_3 + hν ---> O + O_2	k_3 =5.5x 10^{-4} sec^{-1}
Step 4	O + O_3 ---> 2 O_2	A_4 = 8.0 x 10^{-12} ; E_4 = 2060 K
Step 5	O + HO_2 ---> HO + O_2	A_5 = 3.0 x 10^{-11} ; E_4 = -200 K
Step 6	HO + O_3 ---> HO_2 + O_2	A_6 = 1.6 x 10^{-12}; E_6 = 940 K
Step 7	O + NO_2 ---> NO + O_2	A_7= 6.5 x 10^{-12}; E_7 = -120 K
Step 8	NO + O_3 ---> NO_2 + O_2	A_8 = 2 x 10^{-12}; E_8 = 1400 K

Exercise 1. Use the formulas given below and the parameters given to the right of the chemical equations above to calculate the rate constants for the reactions in Steps 2 and 4-8. The convention followed in the answers at the end of this document is to use left bracket-subscripts for rate constants and temperature-dependence parameters. At present, T is globally defined near the end of the document to be 220 K. Also, define the rate constants for Steps 1 and 3.

Arrhenius temperature dependence for second-order reactions (units of k are cm^3/molecule-sec; parameters are A and E, where E actually refers to E_a/R):

$$k(T) = A \cdot e^{-\frac{E}{T}}$$

Temperature dependence for third-order reactions (units of k are cm^6/$molecule^2$-sec; parameters are ko and n):

$$k(T) = ko \cdot \left(\frac{T}{300 \cdot K}\right)^{-n}$$

Exercise 2. Write out the differential rate equations for all seven constituents appearing in Steps 1-8, above. Use the calculus palette to obtain the d/dt symbol and use the control-equals sign. The convention throughout this document is to use the period-subscript for chemical formulas and the left bracket-subscript for rate constants.

Exercise 3. Define a vector y which is filled with elements y_i that represent the initial concentrations of all 7 species whose rates of change are being considered above. Use the matrix palette and define a 7-row, 1-column matrix. Set it up so that the elements y_0, y_1, y_2, y_3, y_4, y_5 and y_6 correspond to the initial concentrations of O, O_2, O_3, HO_2, HO, NO_2 and NO, which are given the variable names initO, $initO_2$, $initO_3$, $initHO_2$, initHO, $initNO_2$ and initNO, respectively. Be sure to use the period-subscript in the chemical formulas, or you will run into trouble later. As in Part I, the actual initial concentrations will be entered with the global definition feature, at the bottom of the document near the plot of concentrations versus time.

y

Exercise 4. Define a seven-element equation vector D(t,y) whose elements describe the initial rates of change of each species. As in Part I of the document, the elements of the vector are just the right-hand sides of the differential equations you wrote above, with mathcad-friendly y_i's in place of O, O_2, etc.

D(t,y)

Exercise 5. Define the 7-row, 8-column matrix J(t,y), in which the first column represents the partial derivatives with respect to t (time) of the functions in the D vector. The second column represents the partial derivatives with respect to y_0 of the functions in the D vector. The third column represents the partial derivatives with respect to y_1 of the functions in the D vector, and so on out to the eighth column (d D/dy_7). This may be easier to write out on paper first.

$J(t, y)$

As in the companion Part I document, we will use the Stiffr numerical method to solve the system of coupled differential equations. This solver function requires six inputs or arguments: Stiffr(y, 0, tmax, npts, D, J), where y is the y-vector of initial concentration values defined above, 0 is the starting time (the time for which the initial concentration values apply), tmax is the ending time, npts is the number of points (beyond the inital point) at which the solution is to be approximated, the D vector is defined above and the J matrix is defined above. Later in the document, you will be asked to define tmax and npts using the global definition feature. The output from Stiffr is stored as "answers," as shown below. Once the template is all set up and the solver has finished solving, you can use the regular equals sign to demonstrate that answers is a matrix in which the first column is time and the subsequent columns give the concentrations of the seven species at each time.

$answers := Stiffr(y, 0, tmax, npts, D, J)$

Exercise 6. Break the answers matrix apart into columns (vectors). The first column (which mathcad calls the zeroth column) in the answers matrix is the series of time values for which concentrations have been calculated. This will become the data used on the x-axis of a plot of concentrations versus time. As shown below, this column is stored with the vector name "t". Follow the same strategy to store the second through eighth columns as the species concentrations (O, O_2, O_3, etc.) To get the symbol <>, use control-6 or go to the matrices palette. Remember to use the period subscript for the chemical formula names!

$t := answers^{\langle 0 \rangle}$

$O := answers^{\langle 1 \rangle}$

Exercise 7. Define the variables tmax and npts with a global definition (triple equals sign), since these two variables are often changed during modelling. To access the triple equals sign for this "global definition" feature, use the Evaluation and Boolean palette or the keystroke shift-tilde (~). Choose reasonable numerical values (recall that tmax is in seconds and npts directly affects the time it takes to solve the problem.)

tmax

npts

Exercise 8. Insert plots that show the concentrations of all species as a function of time, as calculated by the Stiffr solver and stored as vectors in Exercise 6, above. Under the Graphics menu, choose "Create X-Y plot." The x-axis variable is t_i (use the left-bracket subscript) and the y-axis variables are the species concentrations (all with left-bracket subscript i's.) Multiple y-variables can be entered by following the variable name with a comma, but be sure to use the up arrow to select both the variable and the subscript before typing the comma. Before the plot will appear, you will need to define the counter-variable, i, so that it ranges from 0 to npts-1 (0 followed by a semicolon followed by npts-1 will define your range). Double-clicking on an axis allows you to choose to autoscale the plots or change from logarithmic to linear plots. A single click on an axis will bring up the upper and lower limits, which can be modified to rescale the plot. In addition to a single plot with all species displayed on a logarithmic y-axis scale, make individual plots for each of the species so that you can avoid the flattening effect of the logarithmic axis scale.

Exercise 9. Define the temperature, total pressure (number density) and initial concentrations using the global definition feature. For your convenience, rate constants, temperature, pressure and steady state concentrations reported at an altitude of 25 km are shown below with the control equals sign. As such, they can't be used in the calculation, which means that you can keep them as a guide as you make changes.

$T = 220 \cdot K$

$M = 9 \cdot 10^{17}$

$initO = 10^{7}$

$initO_2 = 2 \cdot 10^{17}$

$initO_3 = 7.00 \cdot 10^{12}$

$initHO_2 = 2 \cdot 10^{7}$

$initHO = 3 \cdot 10^{6}$

$initNO_2 = 1 \cdot 10^{9}$

$initNO = 8 \cdot 10^{8}$

$k_1 = 3 \cdot 10^{-12}$

$k_2 = 1.2 \cdot 10^{-33}$

$k_3 = 5.5 \cdot 10^{-4}$

$k_4 = 6.9 \cdot 10^{-16}$

$k_5 = 7.4 \cdot 10^{-11}$

$k_6 = 2.2 \cdot 10^{-14}$

$k_7 = 1.1 \cdot 10^{-11}$

$k_8 = 3.4 \cdot 10^{-15}$

Exercise 10. Solve for the photostationary state (pss) concentrations of all seven species. Solving for seven unknowns requires seven simultaneous equations. First, as done below for O, use the initial concentrations of all nitrogen and hydrogen-containing species to write mass balance equations for N and H. Store the values as totalnitrogen and totalhydrogen, respectively.

Define guess values for the seven photostationary state concentrations, as shown for O (given the variable name pssO). The initial values used for the differential equation solver are generally good guess values.

Under the "Given," write the totaloxygen, totalnitrogen and totalhydrogen expressions using the photostationary state variable names and the control equals sign, as shown for totaloxygen. This provides three equations; four more are needed. Write rate equations for four of the constituents and use the control equals sign to set them equal to zero, as shown for $pssO_3$. (The answers at the end of the document use O_2, O_3, HO_2 and NO_2.) When seven equations have been appropriately defined, type the following command (followed by a regular equals sign) and Mathcad will solve the system of equations and display a vector containing the equilibrium values for all seven species. As shown below, the results of this command can also be stored in a matrix. The numerical values can then be displayed by copying the matrix into a blank spot, followed by a regular equals sign.

find(pssO, $pssO_2$, $pssO_3$, pssNO, $pssNO_2$, pssHO, $pssHO_2$)=

$$totaloxygen := initO + 2 \cdot initO_2 + 3 \cdot initO_3 + 2 \cdot initHO_2 + initHO + 2 \cdot initNO_2 + initNO$$

totaloxygen =

totalnitrogen

totalhydrogen

Guess values for photostationary state concentrations:

pssO := initO

Given

$$pssO + 2 \cdot pssO_2 + 3 \cdot pssO_3 + pssHO + 2 \cdot pssHO_2 + pssNO + 2 \cdot pssNO_2 = totaloxygen$$

$$-k_3 \cdot pssO_3 + k_2 \cdot M \cdot pssO \cdot pssO_2 - k_4 \cdot pssO \cdot pssO_3 - k_6 \cdot pssHO \cdot pssO_3 - k_8 \cdot pssNO \cdot pssO_3 = 0$$

$$\begin{bmatrix} pssO \\ pssO_2 \\ pssO_3 \\ pssNO \\ pssNO_2 \\ pssHO \\ pssHO_2 \end{bmatrix} := find(pssO, pssO_2, pssO_3, pssNO, pssNO_2, pssHO, pssHO_2)$$

Exercise 11. What can you discover about this system? Which cycle of reactions is more important, the HO_x or NO_x cycle? How long does it take to reach the photostationary state situation? What sorts of effects do initial conditions have on the time it takes to reach the photostationary state? Do the photostationary state values agree with the "atmospherically reasonable" values for the initial conditions taken from the JPL reference, or does it appear that other reactions must be considered as well? What other questions can you devise and answer?

Mastery Exercise:

Modify this document to incorporate the following ClO_x reactions, with associated rate and initial concentration information.

Step 9	O + ClO ---> Cl + O_2	A_{10} = 3.0 x 10^{-11}; E_{10} = -70 K
Step 10	Cl + O_3 ---> ClO + O_2	A_{11} = 2.9 x 10^{-11}; E_{11} = 260 K

$Cl = 5\cdot10^4$ $\qquad ClO = 1\cdot10^8$

For your information only: CF_2Cl_2 ---> Cl + CF_2Cl $k_9 = 1 \times 10^{-8}\ sec^{-1}$; $CF2Cl2 = 3 \cdot 10^8$

Reference for all data cited herein:

"*Chemical Kinetics and Photochemical Data for Use in Stratospheric Modelling*," Evaluation Number 12, Jet Propulsion Laboratory: Pasadena, 1997 (JPL Publication 97-4)

Copies of this document are available electronically at the following URL:

http://remus.jpl.nasa.gov/jpl97/

Hardcopies of the 274-page document can be ordered for approximately $50 through the NASA STI Bibliographic Database. For information about this option, go to URL:

http://www.sti.nasa.gov/casitrs.html

and input either the document ID number (19970037557) or the document accession number (97N31001) into the accession number field to obtain pricing and ordering information and to read the full citation for this document.

Answers to Exercises

Exercise 1. Use the appropriate formulas and parameters to calculate the rate constants for the second and third-order reactions in Steps 2 and 4-8. Enter the rate constants for Steps 1 and 3.
Note: To avoid a bug in Mathcad 6.0 that is related to the use of the left-bracket subscripts for the rate constants, the rate constants for Steps 1 and 3 are triply-defined here, above the calculated rate constants for Steps 2 and 4-8. In Mathcad 8.0 the triple-definition statements can be moved down beside the graphs so that they can be changed more easily.

$$k_1 \equiv 3\cdot 10^{-12}$$

$$k_3 \equiv 5.5\cdot 10^{-4}$$

$$ko_2 := 6.0\cdot 10^{-34}$$

$$n_2 := 2.3$$

$$k_2 := ko_2\cdot\left(\frac{T}{300\cdot K}\right)^{-n_2}$$

$$k_2 = 1.224498\cdot 10^{-33}$$

$$E_4 := 2060\cdot K$$

$$A_4 := 8.0\cdot 10^{-12}$$

$$k_4 := A_4\cdot e^{-\frac{E_4}{T}}$$

$$k_4 = 6.863006\cdot 10^{-16}$$

$$E_5 := -200\cdot K$$

$$A_5 := 3.0\cdot 10^{-11}$$

$$k_5 := A_5\cdot e^{-\frac{E_5}{T}}$$

$$k_5 = 7.446195\cdot 10^{-11}$$

$$E_6 := 940\cdot K$$

$$A_6 := 1.6\cdot 10^{-12}$$

$$k_6 := A_6\cdot e^{-\frac{E_6}{T}}$$

$$k_6 = 2.230992\cdot 10^{-14}$$

$$E_7 := -120\cdot K$$

$$A_7 := 6.5\cdot 10^{-12}$$

$$k_7 := A_7\cdot e^{-\frac{E_7}{T}}$$

$$k_7 = 1.121505\cdot 10^{-11}$$

$$E_8 := 1400\cdot K$$

$$A_8 := 2.0\cdot 10^{-12}$$

$$k_8 := A_8\cdot e^{-\frac{E_8}{T}}$$

$$k_8 = 3.446179\cdot 10^{-15}$$

Exercise 2. Write out the differential rate equations for all seven constituents appearing in Steps 1-8, above. Use the calculus palette to obtain the d/dt symbol and use the control-equals sign. The convention throughout this document is to use the period-subscript for chemical formulas and the left bracket-subscript for rate constants.

$$\frac{d}{dt}O = 2\cdot k_1\cdot O_2 - k_2\cdot M\cdot O\cdot O_2 + k_3\cdot O_3 - k_4\cdot O\cdot O_3 - k_5\cdot O\cdot HO_2 - k_7\cdot O\cdot NO_2$$

$$\frac{d}{dt}O_2 = -k_1\cdot O_2 - k_2\cdot M\cdot O\cdot O_2 + k_3\cdot O_3 + 2\cdot k_4\cdot O\cdot O_3 + k_5\cdot O\cdot HO_2 + k_6\cdot HO\cdot O_3 + k_7\cdot O\cdot NO_2 + k_8\cdot NO\cdot O_3$$

$$\frac{d}{dt}O_3 = -k_3\cdot O_3 + k_2\cdot M\cdot O\cdot O_2 - k_4\cdot O\cdot O_3 - k_6\cdot HO\cdot O_3 - k_8\cdot NO\cdot O_3$$

$$\frac{d}{dt}HO_2 = -k_5\cdot O\cdot HO_2 + k_6\cdot HO\cdot O_3$$

$$\frac{d}{dt}HO = k_5\cdot O\cdot HO_2 - k_6\cdot HO\cdot O_3$$

$$\frac{d}{dt}NO_2 = -k_7\cdot O\cdot NO_2 + k_8\cdot NO\cdot O_3$$

$$\frac{d}{dt}NO = k_7\cdot O\cdot NO_2 - k_8\cdot NO\cdot O_3$$

Exercise 3. Define a vector y which is filled with elements y_i that represent the initial concentrations of all 7 species whose rates of change are being considered above. Use the matrix palette and define a 7-row, 1-column matrix. Set it up so that the elements y_0, y_1, y_2, y_3, y_4, y_5 and y_6 correspond to the initial concentrations of O, O_2, O_3, HO_2, HO, NO_2 and NO, which are given the variable names initO, $initO_2$, $initO_3$, $initHO_2$, initHO, $initNO_2$ and initNO, respectively. Be sure to use the period-subscript in the chemical formulas, or you will run into trouble later. As in Part I, the actual initial concentrations will be entered with the global definition feature, at the bottom of the document near the plot of concentrations versus time.

$$y := \begin{bmatrix} initO \\ initO_2 \\ initO_3 \\ initHO_2 \\ initHO \\ initNO_2 \\ initNO \end{bmatrix}$$

Exercise 4. Define a seven-element equation vector D(t,y) whose elements describe the initial rates of change of each species. As in Part I of the document, the elements of the vector are just the right-hand sides of the differential equations you wrote above, with mathcad-friendly y_i's in place of O, O_2, etc.

$$D(t,y) := \begin{bmatrix} 2\cdot k_1\cdot y_1 - k_2\cdot M\cdot y_0\cdot y_1 + k_3\cdot y_2 - k_4\cdot y_0\cdot y_2 - k_5\cdot y_0\cdot y_3 - k_7\cdot y_0\cdot y_5 \\ -k_1\cdot y_1 - k_2\cdot M\cdot y_0\cdot y_1 + k_3\cdot y_2 + 2\cdot k_4\cdot y_0\cdot y_2 + k_5\cdot y_0\cdot y_3 + k_6\cdot y_4\cdot y_2 + k_7\cdot y_0\cdot y_5 + k_8\cdot y_6\cdot y_2 \\ -k_3\cdot y_2 + k_2\cdot M\cdot y_0\cdot y_1 - k_4\cdot y_0\cdot y_2 - k_6\cdot y_4\cdot y_2 - k_8\cdot y_6\cdot y_2 \\ -k_5\cdot y_0\cdot y_3 + k_6\cdot y_4\cdot y_2 \\ k_5\cdot y_0\cdot y_3 - k_6\cdot y_4\cdot y_2 \\ -k_7\cdot y_0\cdot y_5 + k_8\cdot y_6\cdot y_2 \\ k_7\cdot y_0\cdot y_5 - k_8\cdot y_6\cdot y_2 \end{bmatrix}$$

Exercise 5. Define the 7-row, 8-column matrix J(t,y), in which the first column represents the partial derivatives with respect to t (time) of the functions in the D vector. The second column represents the partial derivatives with respect to y_0 of the functions in the D vector. The third column represents the partial derivatives with respect to y_1 of the functions in the D vector, and so on out to the eighth column (d D/dy_7). This may be easier to write out on paper first.

$$J(t,y) := \begin{bmatrix} 0 & -k_2\cdot M\cdot y_1 - k_4\cdot y_2 - k_5\cdot y_3 - k_7\cdot y_5 & 2\cdot k_1 - k_2\cdot M\cdot y_0 & k_3 - k_4\cdot y_0 & -k_5\cdot y_0 & 0 & -k_7\cdot y_0 & 0 \\ 0 & -k_2\cdot M\cdot y_1 + 2\cdot k_4\cdot y_2 + k_5\cdot y_3 + k_7\cdot y_5 & -k_1 - k_2\cdot M\cdot y_0 & k_3 + 2\cdot k_4\cdot y_0 + k_6\cdot y_4 + k_8\cdot y_6 & k_5\cdot y_0 & k_6\cdot y_2 & k_7\cdot y_0 & k_8\cdot y_2 \\ 0 & k_2\cdot M\cdot y_1 - k_4\cdot y_2 & k_2\cdot M\cdot y_0 & -k_3 - k_4\cdot y_0 - k_6\cdot y_4 - k_8\cdot y_6 & 0 & -k_6\cdot y_2 & 0 & -k_8\cdot y_2 \\ 0 & -k_5\cdot y_3 & 0 & k_6\cdot y_4 & -k_5\cdot y_0 & k_6\cdot y_2 & 0 & 0 \\ 0 & k_5\cdot y_3 & 0 & -k_6\cdot y_4 & k_5\cdot y_0 & -k_6\cdot y_2 & 0 & 0 \\ 0 & -k_7\cdot y_5 & 0 & k_8\cdot y_6 & 0 & 0 & -k_7\cdot y_0 & k_8\cdot y_2 \\ 0 & k_7\cdot y_5 & 0 & -k_8\cdot y_6 & 0 & 0 & k_7\cdot y_0 & -k_8\cdot y_2 \end{bmatrix}$$

answers := Stiffr(y, 0, tmax, npts, D, J)

Exercise 6. Break the answers matrix apart into columns (vectors). The first column (which mathcad calls the zeroth column) in the answers matrix is the series of time values for which concentrations have been calculated. This will become the data used on the x-axis of a plot of concentrations versus time. As shown below, this column is stored with the vector name "t". Follow the same strategy to store the second through eighth columns as the species concentrations (O, O_2, O_3, etc.) To get the symbol <>, use control-6 or go to the matrices palette. Remember to use the period subscript for the chemical formula names!

$t := answers^{\langle 0 \rangle}$

$O := answers^{\langle 1 \rangle}$

$O_2 := answers^{\langle 2 \rangle}$

$O_3 := answers^{\langle 3 \rangle}$

$HO_2 := answers^{\langle 4 \rangle}$

$HO := answers^{\langle 5 \rangle}$

$NO_2 := answers^{\langle 6 \rangle}$

$NO := answers^{\langle 7 \rangle}$

Exercise 7. Define the variables tmax and npts with a global definition (triple equals sign), since these two variables are often changed during modelling. To access the triple equals sign for this "global definition" feature, use the Evaluation and Boolean palette or the keystroke shift-tilde (~).

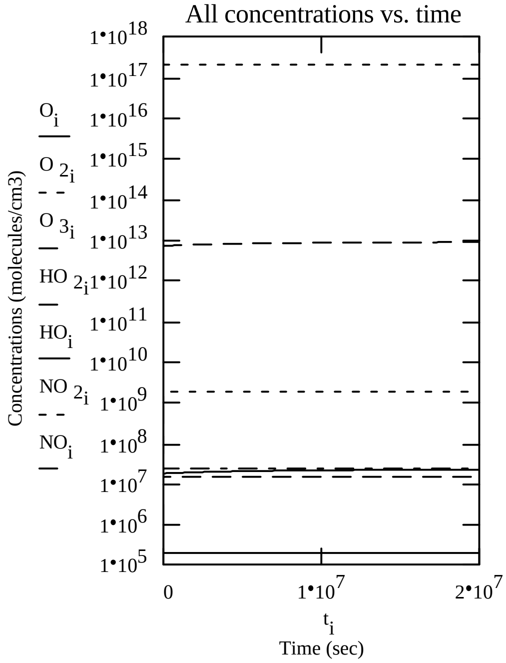
$tmax \equiv 20000000$

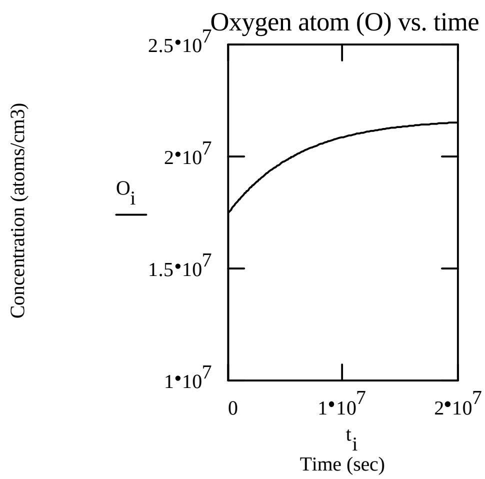
$npts \equiv 1000$

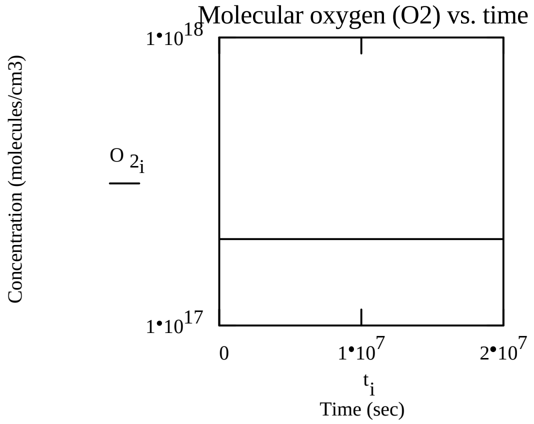
$$\frac{npts}{tmax} = 5 \cdot 10^{-5}$$

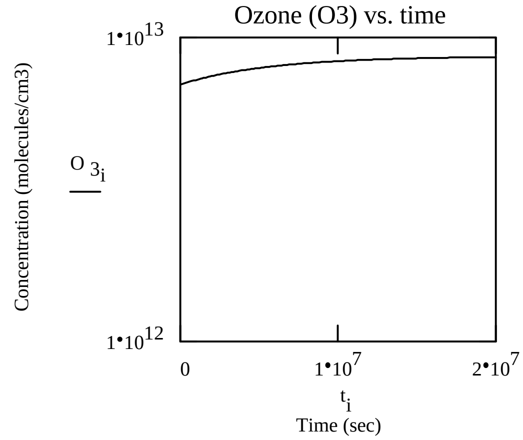
Exercise 8. Insert plots that show the concentrations of all species as a function of time, as calculated by the Stiffr solver and stored as vectors in Exercise 6, above. Under the Graphics menu, choose "Create X-Y plot." The x-axis variable is t_i (use the left-bracket subscript) and the y-axis variables are the species concentrations (all with left-bracket subscript i's.) Multiple y-variables can be entered by following the variable name with a comma, but be sure to use the up arrow to select both the variable and the subscript before typing the comma. Before the plot will appear, you will need to define the counter-variable, i, so that it ranges from 0 to npts-1 (0 followed by a semicolon followed by npts-1 will define your range). Double-clicking on an axis allows you to choose to autoscale the plots or change from logarithmic to linear plots. A single click on an axis will bring up the upper and lower limits, which can be modified to rescale the plot. In addition to a single plot with all species displayed on a logarithmic y-axis scale, make individual plots for each of the species so that you can avoid the flattening effect of the logarithmic axis scale.

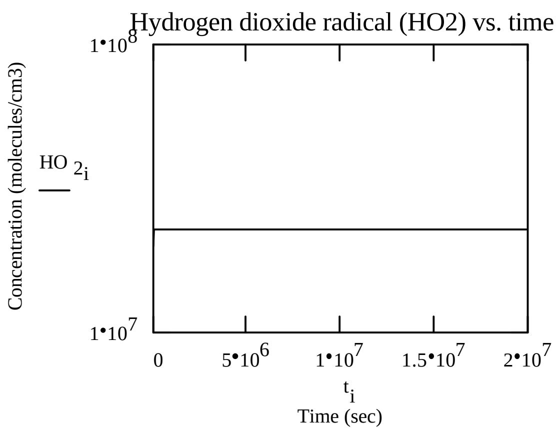
$i := 0 .. npts - 1$

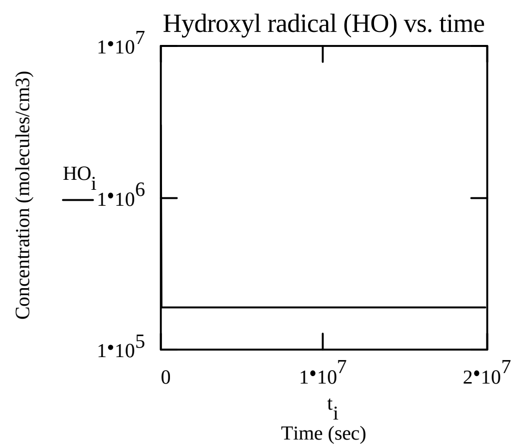


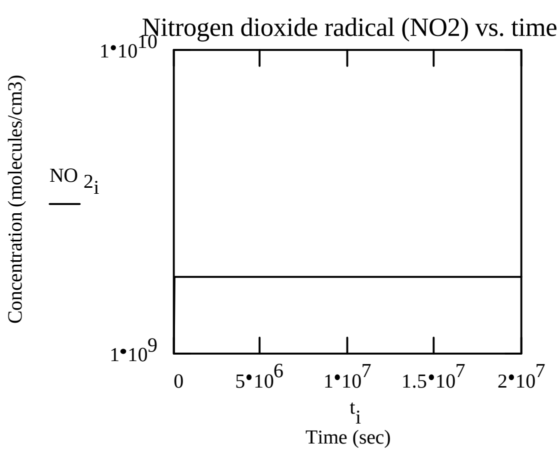


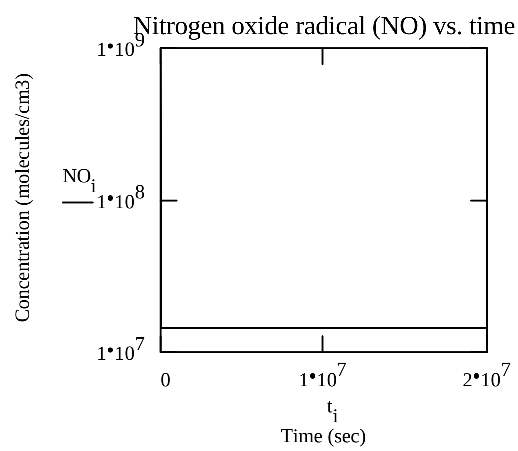

Molecular oxygen (O2) vs. time
1•10^18
1•10^17
Concentration (molecules/cm3)
O 2i
0
1•10^7
2•10^7
ti
Time (sec)


Ozone (O3) vs. time
1•10^13
1•10^12
Concentration (molecules/cm3)
O 3i
0
1•10^7
2•10^7
ti
Time (sec)


Hydrogen dioxide radical (HO2) vs. time
1•10^8
1•10^7
Concentration (molecules/cm3)
HO 2i
0
5•10^6
1•10^7
1.5•10^7
2•10^7
ti
Time (sec)


Hydroxyl radical (HO) vs. time
1•10^7
1•10^6
1•10^5
Concentration (molecules/cm3)
HOi
0
1•10^7
2•10^7
ti
Time (sec)


Nitrogen dioxide radical (NO2) vs. time
1•10^10
1•10^9
Concentration (molecules/cm3)
NO 2i
0
5•10^6
1•10^7
1.5•10^7
2•10^7
ti
Time (sec)


Nitrogen oxide radical (NO) vs. time
1•10^9
1•10^8
1•10^7
Concentration (molecules/cm3)
NOi
0
1•10^7
2•10^7
ti
Time (sec)

Exercise 9. Define the temperature, total pressure (number density) and initial concentrations using the global definition feature. For your convenience, the temperature, pressure, rate constants and steady state concentrations reported at an altitude of 25 km are shown (at the left) below with the control equals sign. As such, they can't be used in the calculation, which means that you can keep them as a guide as you make changes. The rate constants entered and calculated above are also displayed in the right-hand column below, for completeness.

Reference values of model variables are given in these two columns.

$T = 220 \cdot K$

$M = 9 \cdot 10^{17}$

$initO = 10^{7}$

$initO_2 = 2 \cdot 10^{17}$

$initO_3 = 7.00 \cdot 10^{12}$

$initHO_2 = 2 \cdot 10^{7}$

$initHO = 3 \cdot 10^{6}$

$initNO_2 = 1 \cdot 10^{9}$

$initNO = 8 \cdot 10^{8}$

$k_1 = 3 \cdot 10^{-12}$

$k_2 = 1.2 \cdot 10^{-33}$

$k_3 = 5.5 \cdot 10^{-4}$

$k_4 = 6.9 \cdot 10^{-16}$

$k_5 = 7.4 \cdot 10^{-11}$

$k_6 = 2.2 \cdot 10^{-14}$

$k_7 = 1.1 \cdot 10^{-11}$

$k_8 = 3.4 \cdot 10^{-15}$

Global definitions of model variables are given in the middle two columns, below. These can be moved up beside the graphs for ease in making changes.

$T \equiv 220 \cdot K$

$M \equiv 9 \cdot 10^{17}$

$initO \equiv 10^{7}$

$initO_2 \equiv 2 \cdot 10^{17}$

$initO_3 \equiv 7.00 \cdot 10^{12}$

$initHO_2 \equiv 2 \cdot 10^{7}$

$initHO \equiv 3 \cdot 10^{6}$

$initNO_2 \equiv 1 \cdot 10^{9}$

$initNO \equiv 8 \cdot 10^{8}$

Displayed values of rate constants:

$k_1 = 3 \cdot 10^{-12}$

$k_2 = 1.22449769 \cdot 10^{-33}$

$k_3 = 5.5 \cdot 10^{-4}$

$k_4 = 6.863006 \cdot 10^{-16}$

$k_5 = 7.446195 \cdot 10^{-11}$

$k_6 = 2.230992 \cdot 10^{-14}$

$k_7 = 1.121505 \cdot 10^{-11}$

$k_8 = 3.446179 \cdot 10^{-15}$

Exercise 10. Solve for the photostationary state (pss) concentrations of all seven species. Solving for seven unknowns requires seven simultaneous equations. First, as done below for O, use the initial concentrations of all nitrogen and hydrogen-containing species to write mass balance equations for N and H. Store the values as totalnitrogen and totalhydrogen, respectively.

Define guess values for the seven photostationary state concentrations, as shown for O (given the variable name pssO). The initial values used for the differential equation solver are generally good guess values.

Under the "Given," write the totaloxygen, totalnitrogen and totalhydrogen expressions using the photostationary state variable names and the control equals sign, as shown for totaloxygen. This provides three equations; four more are needed. Write rate equations for four of the constituents and use the control equals sign to set them equal to zero, as shown for $pssO_3$. (The answers below use O_2, O_3, HO_2 and NO_2.) When seven equations have been appropriately defined, type the following command (followed by a regular equals sign) and Mathcad will solve the system of equations and display a vector with the equilibrium values for all seven species. As shown below, the results of this command can also be stored in a matrix. The numerical values can then be displayed by copying the matrix into a blank spot, followed by a regular equal sign.

find(pssO, $pssO_2$, $pssO_3$, pssNO, $pssNO_2$, pssHO, $pssHO_2$)=

$$totaloxygen := initO + 2\cdot initO_2 + 3\cdot initO_3 + initHO + 2\cdot initHO_2 + initNO + 2\cdot initNO_2$$

$$totaloxygen = 4.00021\cdot 10^{17}$$

$$totalnitrogen := initNO + initNO_2$$

$$totalnitrogen = 1.800000000000000\cdot 10^{9}$$

$$totalhydrogen := initHO + initHO_2$$

$$totalhydrogen = 2.300000000000000\cdot 10^{7}$$

Guess values for photostationary state concentrations:

$$\begin{bmatrix} pssO \\ pssO_2 \\ pssO_3 \\ pssNO \\ pssNO_2 \\ pssHO \\ pssHO_2 \end{bmatrix} := \begin{bmatrix} initO \\ initO_2 \\ initO_3 \\ initNO \\ initNO_2 \\ initHO \\ initHO_2 \end{bmatrix}$$

Given

$$pssO + 2\cdot pssO_2 + 3\cdot pssO_3 + pssHO + 2\cdot pssHO_2 + pssNO + 2\cdot pssNO_2 = totaloxygen$$

$$pssNO + pssNO_2 = totalnitrogen$$

$$pssHO + pssHO_2 = totalhydrogen$$

$$\begin{pmatrix} -k_1\cdot pssO_2 - k_2\cdot M\cdot pssO\cdot pssO_2 + k_3\cdot pssO_3 + 2\cdot k_4\cdot pssO\cdot pssO_3 \ldots \\ + k_5\cdot pssO\cdot pssHO_2 \ldots \\ + k_6\cdot pssHO\cdot pssO_3 \end{pmatrix} + k_7\cdot pssO\cdot pssNO_2 + k_8\cdot pssNO\cdot pssO_3 = 0$$

$$-k_3\cdot pssO_3 + k_2\cdot M\cdot pssO\cdot pssO_2 - k_4\cdot pssO\cdot pssO_3 - k_6\cdot pssHO\cdot pssO_3 - k_8\cdot pssNO\cdot pssO_3 = 0$$

$$-k_5\cdot pssO\cdot pssHO_2 + k_6\cdot pssHO\cdot pssO_3 = 0$$

$$-k_7\cdot pssO\cdot pssNO_2 + k_8\cdot pssNO\cdot pssO_3 = 0$$

$$\begin{bmatrix} pssO \\ pssO_2 \\ pssO_3 \\ pssNO \\ pssNO_2 \\ pssHO \\ pssHO_2 \end{bmatrix} := find(pssO, pssO_2, pssO_3, pssNO, pssNO_2, pssHO, pssHO_2)$$

Photostationary state values:

$$\begin{bmatrix} pssO \\ pssO_2 \\ pssO_3 \\ pssNO \\ pssNO_2 \\ pssHO \\ pssHO_2 \end{bmatrix} = \begin{bmatrix} 2.167365\cdot 10^{7} \\ 1.999975\cdot 10^{17} \\ 8.684398\cdot 10^{12} \\ 1.450157\cdot 10^{7} \\ 1.785498\cdot 10^{9} \\ 1.900001\cdot 10^{5} \\ 2.281\cdot 10^{7} \end{bmatrix}$$

Final (tmax) values from the differential equation solver:

$$\begin{bmatrix} O_{npts-1} \\ O2_{npts-1} \\ O3_{npts-1} \\ NO_{npts-1} \\ NO2_{npts-1} \\ HO_{npts-1} \\ HO2_{npts-1} \end{bmatrix} = \begin{bmatrix} 2.152178\cdot 10^{7} \\ 1.999976\cdot 10^{17} \\ 8.623536\cdot 10^{12} \\ 1.45016\cdot 10^{7} \\ 1.785498\cdot 10^{9} \\ 1.900004\cdot 10^{5} \\ 2.281\cdot 10^{7} \end{bmatrix}$$

As described in the Part I document, the values in the matrices above can be compared to determine whether or not the differential equations have been solved with a long enough tmax to reach the photostationary state.

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