Modeling Stratospheric Ozone Kinetics, Part I ©

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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 had at least a year of calculus and have completed the Mathcad tutorial. In addition, it is recommended that you study the chemical kinetics sections of a physical chemistry textbook as you work through this document. This document requires Mathcad 6.0+ or later (the professional version, which has specialized differential equations solvers).

Goal: The pair of documents, Modeling Stratospheric Ozone Kinetics Part I and Part II, is designed to lead students into modeling the kinetics of stratospheric ozone reactions. Part I focuses on the mechanics of the modeling method and considers only the Chapman cycle of reactions for stratospheric ozone. In the companion document, 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. write differential rate expressions for species involved in a series of chemical reactions
2. set up and numerically solve systems of differential equations to show the time evolution of a chemical system
3. determine the effects of varying rate constants and initial concentrations
4. recognize and understand the Chapman cycle that controls ozone concentrations in the stratosphere

Introduction: The "ozone layer" is a region of the atmosphere that contains a steady state concentration of ozone, resulting from a set of reactions occurring in the stratosphere. Driven by a constant input of solar energy, this critical set of reactions helps to maintain a temperature inversion in the stratosphere and to protect the surface of the earth from ultraviolet wavelengths of solar radiation. 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/)).

This Mathcad document serves as an introduction to numerical solutions of complex rate laws and kinetic modelling, using stratospheric ozone chemistry as an example. Students learn how to write differential rate laws for each component to be included, define initial concentrations and rate constants, enter the set of differential equations as a matrix for use with a built-in differential equation solver, and finally generate and graph species concentration profiles over specified time intervals. Specific variables that can be explored in this document include temperature, total pressure, initial component concentrations and rate constants. The reference cited above (or its successor) will be a highly useful resource for advanced modelling studies based on this template.

The thermodynamic quantities, rate constants, activation parameters, stratospheric concentrations and total number density of atmospheric constituents used in this document were taken to the best of the authors' ability from Tables 1 and 2 and Appendices I, II and III in the NASA/JPL document cited above; unless otherwise noted, the values apply at an altitude of 25 km and a temperature of 220 K. Units are shown in the text, but are not used in most of the calculations because the differential equation solver requires unitless inputs.

Sample answers to some of the questions posed in the text are given at the end of the document.

Helpful hints:

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. When you are ready, you can start processing again by choosing "Calculate worksheet" from the Math menu. Alternatively, for a more drastic and long-lasting solution, you can go to the Math menu and turn off the checkmark beside Automatic mode. When automatic mode is de-selected, you must push the F9 key to start EVERY calculation, even seemingly trivial ones. Calculation times of less than one minute are typical for calculations in this worksheet with Mathcad installed on a 120 MHz Pentium.

To make additional space in a Mathcad 6.0+ document, add blank lines by using control-F9. Extra blank lines can be deleted from the document with the keystrokes control-F10.

Check your user manual for performing these operations with Mathcad 7.0 and Mathcad 8.0 versions of the software.

Section 1. Setting up and solving the system of differential equations

We begin by considering the Chapman cycle, the fundamental cycle of reactions that creates the ozone layer. The Chapman cycle, shown in Steps 1-4, involves only oxygen-containing species; each step is discussed in detail below.

Step 1	$O_2 + h\nu \longrightarrow 2\,O$	$k_1 = 3 \times 10^{-12}\ \mathrm{sec}^{-1}$
Step 2	$M + O + O_2 \longrightarrow M + O_3$	$k_2 = 1.2 \times 10^{-33}\ \mathrm{cm}^6/\mathrm{molecule}^2\text{-sec}$
Step 3	$O_3 + h\nu \longrightarrow O + O_2$	$k_3 = 5.5 \times 10^{-4}\ \mathrm{sec}^{-1}$
Step 4	$O + O_3 \longrightarrow 2\,O_2$	$k_4 = 6.9 \times 10^{-16}\ \mathrm{cm}^3/\mathrm{molecule}\text{-sec}$

In Step 1, molecular oxygen is split into two oxygen atoms (diradicals) by "hard" UV light (λ =185 nm to 220 nm; detailed absorption cross-section information is given in reference 1). Solar energy is used to break the bond (ΔH for the reaction is 119.14 kcal/mol; see Appendix I of reference 1). Any leftover energy is imparted as kinetic energy to the two oxygen atoms (which is, by definition, equivalent to modestly heating the system). The rate constant shown is known as a photolysis rate constant or "J-value." It represents an effective first-order rate constant that takes into account the average solar flux and average absorption cross-section.

Step 1 $\quad O_2 + h\nu \longrightarrow 2\,O \quad k_1 = 3 \times 10^{-12}\ \mathrm{sec}^{-1}$

In Step 2, an oxygen atom reacts with an oxygen molecule to form ozone. In thermodynamic terms, this is a spontaneous, exothermic reaction at stratospheric temperatures. For this reaction, ΔH is -25.47 kcal/mol and ΔS is -30.5 cal/mol-K. The energy given off when the reaction occurs is given to the product molecules as kinetic energy, thereby increasing the temperature of the stratosphere. A third body (denoted as M) is required to conserve momentum and allow this reaction to occur. This third body can be any atom or molecule in the stratosphere that can absorb kinetic energy. If a third body is not present to carry away the released energy, the ozone molecule that is formed will simply redissociate. Note the concentration units implied by the form of the termolecular rate constant.

Step 2 $\quad O + O_2 + M \longrightarrow O_3 + M \quad k_2 = 1.2 \times 10^{-33}\ \mathrm{cm}^6/\mathrm{molecule}^2\text{-sec}$

The next reaction, Step 3 below, requires an input of energy to occur because it is the reverse of the spontaneous reaction in Step 2. The reaction proceeds photochemically. Ozone absorbs UV light in the wavelength range 210 nm to 300 nm and splits into an oxygen atom and an oxygen molecule. Again, any energy leftover from the bond-breaking goes into increasing the kinetic energy of the products. Detailed information about absorption cross-sections and the atomic state of the oxygen radical is provided in reference 1 (see the end of this document for references).

Step 3 $\quad O_3 + h\nu \longrightarrow O + O_2 \quad k_3 = 5.5 \times 10^{-4}\ \mathrm{sec}^{-1}$

When the chemically reactive O and O_3 find each other, a spontaneous reaction occurs to produce two oxygen molecules with lots of kinetic energy. This reaction is highly exothermic (ΔH is -93.67 kcal/mol.)

Step 4 $O + O_3 \text{ ---> } 2\,O_2$ $k_4 = 6.9 \times 10^{-16}\ \mathrm{cm^3/molecule\text{-}sec}$

Using this simplified set of stratospheric reactions, it is possible to watch the system evolve toward a steady state condition known as a photostationary state, where light is continually absorbed by the system but chemical species concentrations no longer change with time. Remember, though, that the cycle operates continuously to change UV light into stratospheric warmth.

Exercises:

1. Why is a third body not needed in Step 4?
2. The reactions above represent a chain reaction. Identify the initiation, propagation and termination steps.
3. Add together the two chain propagation steps. What is the overall reaction?
4. What are the units of concentration being used? Why would these units be chosen rather than molarity?
5. Explain how the cycle of reactions operates to warm the stratosphere. Which two reactions are most important for the warming effect? Why?

Now that we have written a series of reactions that occur in the stratosphere, it is possible to write the expressions for the change in each of the species' concentrations with time; i.e., the differential rate expressions. Each of these expressions is called a differential equation, and together they form a coupled system of differential equations. Mathcad is very useful for solving numerically such systems of differential equations. Note that each reaction step contributing to the formation or loss of a particular constituent must be included in the differential rate law for that constituent. For the oxygen atoml, O, reactions 1 and 3 above are formation steps and reactions 2 and 4 are destruction or loss steps. The stoichiometry is included as shown below, and the photon flux is included implicitly in the photolysis rate constants. Note that O_2 denotes "the concentration of O_2." Square brackets for concentration are not shown because Mathcad uses them for a different purpose.

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

Exercise 6:

Stop and write out the differential rate equations for the other two constituents now. Use the calculus palette to find 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. For convenience, the reaction cycle under consideration has been reproduced below. Add and delete extra lined from your Mathcad document as directed in the manual for your version of Mathcad.

Step 1	$O_2 + h\nu \text{--->} 2\,O$	$k_1 = 3 \times 10^{-12}\ sec^{-1}$
Step 2	$M + O + O_2 \text{--->} M + O_3$	$k_2 = 1.2 \times 10^{-33}\ cm^6/molecule^2\text{-}sec$
Step 3	$O_3 + h\nu \text{--->} O + O_2$	$k_3 = 5.5 \times 10^{-4}\ sec^{-1}$
Step 4	$O + O_3 \text{--->} 2\,O_2$	$k_4 = 6.9 \times 10^{-16}\ cm^3/molecule\text{-}sec$

For Mathcad's sake, it is necessary to change from the chemically intuitive formulation of rate equations above to a vector formulation. The first step is to define a vector y which is filled with elements y_i arranged in a vertical stack. The matrix palette is used to define a 3-row, 1-column matrix. The elements y_0, y_1, y_2 correspond to the initial concentrations of O, O_2 and O_3, respectively. For convenience in making changes later, the actual numerical values for the initial concentrations will be globally defined (triple equals sign) at the bottom of the document, right beside a plot of concentrations versus time. The triple equals sign is a way of letting the user specify variables after the point in the document where the variables first have been used in equations. Mathcad initially scans through the document and sets all of the variables that are globally defined, then works stepwise from the beginning to the end of the document. Since the variables called initialO, $initialO_2$ and $initialO_3$ are globally defined (assigned numerical values) below, Mathcad doesn't object when we use them here.

$$y := \begin{bmatrix} initialO \\ initialO_2 \\ initialO_3 \end{bmatrix}$$

Definitions:

y_0 is the initial conc of O
y_1 is the initial conc of O_2
y_2 is the initial conc of O_3

The next step is to make an equation vector D whose elements describe the rates of change of each species. The elements of the vector are just the right-hand sides of the differential equations that you wrote above, with Mathcad-friendly y_i's in place of O, O_2 and O_3. Since the y vector contains the <u>initial</u> concentrations of each component, the equation vector D actually represents the initial rate of change of each of the components with time.

$$D(t,y) := \begin{bmatrix} 2\cdot k_1\cdot y_1 - k_2\cdot M\cdot y_0\cdot y_1 + k_3\cdot y_2 - k_4\cdot y_0\cdot y_2 \\ -k_1\cdot y_1 - k_2\cdot M\cdot y_0\cdot y_1 + k_3\cdot y_2 + 2\cdot k_4\cdot y_0\cdot y_2 \\ -k_3\cdot y_2 + k_2\cdot M\cdot y_0\cdot y_1 - k_4\cdot y_0\cdot y_2 \end{bmatrix}$$

We are soon going to ask Mathcad to solve the system of coupled differential equations represented by D(t,y) above. Symbolic solutions to this system of equations would consist of mathematical functions that describe each of the concentrations as they change with time. However, Mathcad uses a numerical method to solve this system of differential equations, rather than a symbolic method. The numerical method returns the numerical values of the concentrations at user-specified times, rather than the mathematical functions that would allow a user to calculate the concentrations at any time. Mathcad has several choices of built-in functions to solve systems of differential equations. Different functions are good for different types of systems. The particular reaction conditions being considered in this document lend themselves to a specialized differential equation solving method that the Mathcad manual suggests for "stiff" systems. According to Noggle (reference 2), "stiff equations result when a series of fast processes combine to produce a slow overall change." Such conditions can arise from rate constants that have very different orders of magnitude.

An additional matrix that provides information about the system of equations is required as an input when the "stiff" solver is used. This matrix J is shown below. Each column in J represents a set of partial second derivatives of the functions whose first derivatives with respect to time are given in the D vector. This is not as scary as it may sound! The first column of the J matrix represents the partial derivatives with respect to t (time) of the functions in the D vector. Remember that the D vector itself represents a bunch of first derivatives of concentration functions with respect to time (dO_2/dt is the second element, for example). Therefore, the first column of the J matrix represents the second derivative functions with respect to time ($\delta^2 O_2/\delta t^2$ represents the second element of the first column, for example). The second column of the J matrix represents the partial derivatives with respect to y_0 of the functions in the D vector (i.e., the second element of the second column could be represented as $\delta^2 O_2/\delta t \delta y_0$.) The third column represents the partial derivatives with respect to y_1 of the functions in the D vector, and the fourth column represents the partial derivatives with respect to y_2 of the functions in the D vector.

Exercise 7:

Write out the partial derivatives with respect to time, y_0, y_1 and y_2 for each of the elements in the D vector, and verify that your answers agree with the entries in the J matrix here immediately below.

$$J(t,y) := \begin{bmatrix} 0 & -k_2 \cdot M \cdot y_1 - k_4 \cdot y_2 & 2 \cdot k_1 - k_2 \cdot M \cdot y_0 & k_3 - k_4 \cdot y_0 \\ 0 & -k_2 \cdot M \cdot y_1 + 2 \cdot k_4 \cdot y_2 & -k_1 - k_2 \cdot M \cdot y_0 & k_3 + 2 \cdot k_4 \cdot y_0 \\ 0 & k_2 \cdot M \cdot y_1 - k_4 \cdot y_2 & k_2 \cdot M \cdot y_0 & -k_3 - k_4 \cdot y_0 \end{bmatrix}$$

To use the stiff differential equation solver in Mathcad, the user is required to specify the number of points at which the equations will be solved and the starting and ending times. Here, we are starting at t=0 and ending at the user-specified tmax (in seconds, because of the units on the rate constants being used). It's good practice to pay attention to the ratio of npts to tmax because the numerical method may miss interesting fluctuations if you step too quickly through the time interval. (The ratio is "high enough" if the appearance of the solutions doesn't change as you increase the ratio.) The last command below calls on the Stiffr (Rosenbrock) numerical method to solve the equations, and stores the numerical solutions (concentrations of each species at each time for which the equations were solved) in a matrix named "answers".

$npts := 1000$

$tmax := 20000000$

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

$i := 0 .. npts - 1$

This definition of i as the counter variable is useful for plotting the results in a graph, below.

$answers := \mathrm{Stiffr}(y, 0, tmax, npts, D, J)$

Assuming that the calculation has not been interrupted and the lightbulb is no longer flashing, the answers matrix will be displayed below if you remove the extra "m" from the end of the word "answersm." The first column is time, and the second, third and fourth columns represent the concentrations of O, O_2 and O_3, respectively. If the matrix is so big that it blocks your reading of this document, you can temporarily hide it by re-inserting an extra letter at the end of the word "answers". This will make it an undefined variable and the matrix will disappear. To get it back, just remove the extra letter you added.

answersm =

Note: In Mathcad8 set the Format Result Matrix Display style to Automatic before removing the m in answersm shown here to the left

The next set of commands breaks the answers matrix apart into columns (vectors). The first column, the series of time values for which concentrations have been calculated, will become the data used on the x-axis of a plot of concentrations versus time. To get the symbol <>, use control-6 or go to the matrices palette. The second, third and fourth columns are stored as the concentrations of O, O_2 and O_3, respectively. Mathcad will let us plot all three concentrations on the y-axis at the same time.

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

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

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

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

Finally, the moment of truth has arrived! The plots below show the concentrations of all species as a function of time, individually and grouped on a single plot. Double-clicking on the axes allows you to change from logarithmic to linear plots. A single click on the axes will bring up the upper and lower limits, which can be modified to rescale a plot.

Directly above the plots are the global definitions of the variables in the model, including rate constants for each reaction and initial concentrations of each of the chemical species. To access the triple equals sign for this "global definition" feature, use the Evaluation and Boolean palette or the keystroke shift-tilde (~).

For your convenience in "playing around" and changing variables, the chemical equations to which the rate constants correspond have been reproduced below the graphs, along with atmospherically reasonable values for the variables. Note that these have been entered with a control-equals sign (to produce a bold equal sign) so that they do not interact with the calculations and can serve as a constant reference point.

The concentration of M is the total concentration of all stratospheric constituents. This number is essentially independent of the nature of the constituents and the elapsed reaction time, so it is simply entered as the total number density at an altitude of 25 km. We assumed that the ratio of N_2 to O_2 was the same as in the troposphere, and calculated the concentration of O_2 as 20% of the total number density at an altitude of 25 km. The other constituent concentrations were read from plots of trace constituent concentrations versus altitude in Appendix III of reference 1. Rate constants were calculated as described in Section 3 of this template.

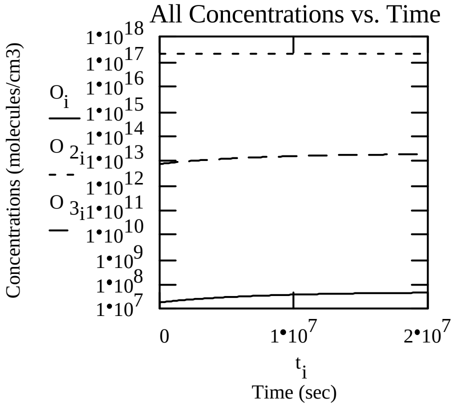
Global definitions of model variables:

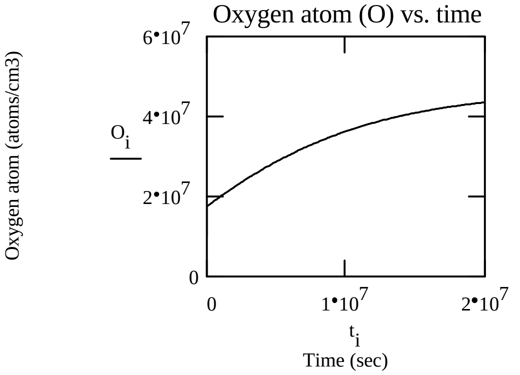
$M \equiv 9 \cdot 10^{17}$ $\quad$ $initialO_2 \equiv 2 \cdot 10^{17}$

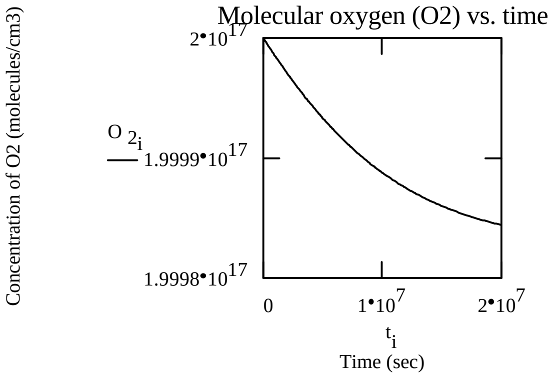
$initialO \equiv 10^{7}$ $\quad$ $initialO_3 \equiv 7.00 \cdot 10^{12}$

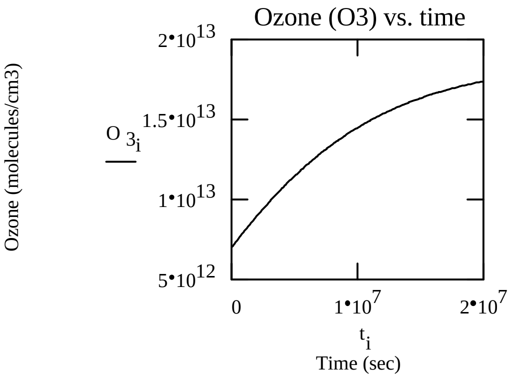
$k_1 \equiv 3 \cdot 10^{-12}$ $\quad$ $k_3 \equiv 5.5 \cdot 10^{-4}$

$k_2 \equiv 1.22 \cdot 10^{-33}$ $\quad$ $k_4 \equiv 6.9 \cdot 10^{-16}$


All Concentrations vs. Time


Oxygen atom (O) vs. time


Molecular oxygen (O2) vs. time


Ozone (O3) vs. time

Step 1	$O_2 \longrightarrow 2\,O$	$k_1 = 3 \times 10^{-12}\ sec^{-1}$
Step 2	$M + O + O_2 \longrightarrow M + O_3$	$k_2 = 1.2 \times 10^{-33}\ cm^6/molecule^2\text{-}sec$
Step 3	$O_3 \longrightarrow O + O_2$	$k_3 = 5.5 \times 10^{-4}\ sec^{-1}$
Step 4	$O + O_3 \longrightarrow 2\,O_2$	$k_4 = 6.9 \times 10^{-16}\ cm^3/molecule\text{-}sec$

$O = 10^{7}$ $\quad$ $M = 9 \cdot 10^{17}$

$O_2 = 2 \cdot 10^{17}$ $\quad$ $T = 220$

$O_3 = 7 \cdot 10^{12}$

These are stratospherically reasonable values of rate constants, concentrations and temperature at an altitude of 25 km.

Exercise 8:

Change the rate constants, one at a time, by a factor of 10. Make your changes by editing the equations with the triple-equals signs. After altering a rate constant, see if the change had a discernible effect on the plots of concentrations. Now return that rate constant to the default value and change another. Make four general statements about trends you observe as you vary conditions. Try to explain the results of this experiment using your knowledge of chain reaction kinetics.

Section 2. Photostationary state (PSS): the "final" solution

The following section shows the use of simultaneous equations to solve for the photostationary state (abbreviated pss) concentrations of the atmospheric constituents (i.e., the long-term steady state concentrations that will persist as long as light continues to be absorbed). This section is useful when you are entering lots of different initial values and trying to see the effects on your model. A quick comparison of the calculated concentration values at the end of the chosen differential equation solver time period with the values calculated below tells you whether or not the system has truly stopped changing; i.e, reached the long-term steady state.

The 'totaloxygen' variable defined below gives the total number of O atoms (either loose or bonded in molecules) per cubic centimeter of atmosphere. Mass balance requires that this number must remain constant. The initial concentrations used below to calculate totaloxygen are defined by the triple-equals signs above, and will be updated each time you change variables above.

The values for the photostationary state variables entered under the "Guess values" subheading are needed to help Mathcad solve the set of simultaneous equations. The values we set for the initial values in the differential equation solver often turn out to be adequate guess values to allow Mathcad to find the solutions, so they are used (and displayed numerically) below.

Under the "Given," Mathcad is given three equations that contain three unknowns (the photostationary state values for O, O_2 and O_3.) The first equation just states the fact that totaloxygen remains constant at the value shown above the Given. The second and third equations require that dO_2/dt and dO_3/dt be equal to 0, i.e, that the concentrations of O_2 and O_3 are no longer changing with time. The find function solves the system of three equations and three unknowns and returns a vector of concentrations that satisfy the conditions we imposed. These are the photostationary state conditions.

$\text{totaloxygen} := \text{initialO} + 2\cdot\text{initialO}_2 + 3\cdot\text{initialO}_3$ $\quad$ $\text{totaloxygen} = 4.0002100001\cdot10^{17}$

Guess values:

$\text{pssO} := \text{initialO}$ $\quad$ $\text{pssO} = 1\cdot10^{7}$

$\text{pssO}_2 := \text{initialO}_2$ $\quad$ $\text{pssO}_2 = 2\cdot10^{17}$

$\text{pssO}_3 := \text{initialO}_3$ $\quad$ $\text{pssO}_3 = 7\cdot10^{12}$

Given

$$\text{pssO} + 2\cdot\text{pssO}_2 + 3\cdot\text{pssO}_3 = \text{totaloxygen}$$

$$-k_1\cdot\text{pssO}_2 - k_2\cdot M\cdot\text{pssO}\cdot\text{pssO}_2 + k_3\cdot\text{pssO}_3 + 2\cdot k_4\cdot\text{pssO}\cdot\text{pssO}_3 = 0$$

$$-k_3\cdot\text{pssO}_3 + k_2\cdot M\cdot\text{pssO}\cdot\text{pssO}_2 - k_4\cdot\text{pssO}\cdot\text{pssO}_3 = 0$$

$$\begin{bmatrix}\text{pssO}\\ \text{pssO}_2\\ \text{pssO}_3\end{bmatrix} := \text{find}\left(\text{pssO}, \text{pssO}_2, \text{pssO}_3\right)$$

Here, the photostationary state concentration values resulting from the "find" command are stored in a matrix.

To compare the photostationary state values generated by the simultaneous equation solver with the final values from the differential equation solver, we need to display the latter values in a convenient format. For example, to look at the last value of O_3 generated by the differential equation solver, you can type O_3 using the period-subscript, then use the left-bracket-subscript to type "npts-1" (this gives the last value, at tmax) and the regular equals sign. This has been done below for each of the components using a matrix format. Thus, it is very easy to do a line-by-line comparion of the tmax results from the differential equation solver and the photostationary state results obtained from the simultaneous equation solver.

If the component concentrations calculated by the two methods and displayed below are equal, then a long enough tmax has been used in the differential equation solver to allow the system to reach the photostationary state. In the case shown below, the system has not quite reached the photostationary state. This fact is also evident in the graphs that show the individual species concentrations, for they are still changing with time at the end of the period for which the differential equations have been solved.

Differential equation solutions at tmax:

$$\begin{bmatrix} O_{npts-1} \\ O2_{npts-1} \\ O3_{npts-1} \end{bmatrix} = \begin{bmatrix} 4.354746240385475 \cdot 10^{7} \\ 1.999844228912582 \cdot 10^{17} \\ 1.738472797901555 \cdot 10^{13} \end{bmatrix}$$

Photostationary state values from simultaneous equation solver:

$$\begin{bmatrix} pssO \\ pssO2 \\ pssO3 \end{bmatrix} = \begin{bmatrix} 4.666905102204752 \cdot 10^{7} \\ 1.999825535371536 \cdot 10^{17} \\ 1.863096300790827 \cdot 10^{13} \end{bmatrix}$$

Exercises:

9. How quickly is the photostationary state reestablished if the initial ozone concentration drops by a factor of 10? What happens to the concentrations if the atmosphere starts with only O_2 and no O or ozone? How long does the system take to reach the photostationary state in this case?

Hints: You may need to change tmax to answer these questions. To avoid errors in logarithmic graphs, enter the concentrations of O and O_3 as 0.1 molecule/cm^3 rather than zero. If you make changes to the model and the given/find solver has trouble finding a solution, try improving your guess values by using the values of the variables near the end of the time period covered by the differential equation solver (e.g., the final values shown in the left-hand matrix equation above.) For instance, when we set the initial ozone concentration to 7x10^{11} to answer the first question in this exercise, the solver failed when the initial values were used as guess values. However, simply changing the oxygen atom guess statement to

pssO=5*initialO

was adequate to help the solver find a solution.

10. Explore the effects of changing the total concentration of atmospheric species, M. Note that you can either change M alone (equivalent to adding or deleting species that are not involved in the chemical reactions) or change the M and O_2 concentrations in combination so that O_2 remains approximately 20% of M (equivalent to changing the pressure by changing the volume of the air mass).

11. What is the effect of increasing or decreasing the number of points and the time scale? Discuss the tradeoffs involved with changing npts and tmax. At what values of npts and tmax do you consider the results to be reliable?

Section 3. A closer look at the rate constants

The temperature of the stratosphere varies considerably with altitude, and the rate constants for the reactions involved vary considerably with temperature. For bimolecular reactions, the JPL source actually reports Arrhenius factors, rather than the rate constants themselves. Substitution of the activation energy and pre-exponential terms into the Arrhenius equation gives the rate constant as a function of temperature. For example, the activation energy for the reaction corresponding to k_4 is given as 2060 (the value given is actually E_a/R, and therefore has units of K) and the preexponential factor is $8.0\text{x}10^{-12}$ cm^3/molecule-sec. Once these variables are defined and the Arrhenius equation is entered, the value of k_4 will be automatically updated as the variable T (temperature in Kelvins) is changed. For convenience, the temperature is globally defined just above the plots at the end of this section.

$$E_4 := 2060 \cdot K$$

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

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

Note that E_4 really represents E_a/R for the reaction in step 4 of our kinetic scheme.

$$k_4 = 6.863006081260039 \cdot 10^{-16}$$

The regular equals sign is used to ask the program to display the calculated value of k_4.

For the termolecular reaction incorporated into this model, the temperature dependence is calculated using a two-parameter equation that is different from the Arrhenius equation and unfamiliar to most undergraduate physical chemistry students. The parameters given in the JPL reference for reaction 2 are the low-pressure limiting rate constant, $k_o = 6.0 \text{ x } 10^{-34}$ $\text{cm}^6/\text{molecule}^2$-sec and n = 2.3 (unitless).

$$k_0 := 6.0 \cdot 10^{-34}$$

k_0 and n are the two parameters tabulated in the JPL reference.

$$n := 2.3$$

$$k_2 := k_0 \cdot \left(\frac{T}{300 \cdot K}\right)^{-n}$$

$$k_2 = 1.224497690500591 \cdot 10^{-33}$$

This equation calculates the rate constant using the temperature-dependent equation given in the reference work. Since temperature is defined above in units of Kelvin, the 300 appearing in the denominator must also have units of Kelvin.

Rates for photochemical reactions are also unfamiliar to many undergraduate physical chemistry students. The reaction rate will depend on the solar flux and the concentration of the photoreactive constituent, in addition to the match between the absorption spectrum of the photoreactive constituent and the emission spectrum of the light (sunlight, in this case.) The JPL reference is kind enough to give tables of effective unimolecular rate constants that incorporate average solar fluxes and spectral information. These are treated as temperature-independent constants in the present document.

Note that the k's defined with triple-equals signs beside the graphs in Section I are the ones used by the differential equation solver in that section. The numerical integration steps and concentration plots are reproduced below so that you are able to visualize the effects of altering the k's by adjusting T in this section.

$$D(t,y) := \begin{bmatrix} 2\cdot k_1\cdot y_1 - k_2\cdot M\cdot y_0\cdot y_1 + k_3\cdot y_2 - k_4\cdot y_0\cdot y_2 \\ -k_1\cdot y_1 - k_2\cdot M\cdot y_0\cdot y_1 + k_3\cdot y_2 + 2\cdot k_4\cdot y_0\cdot y_2 \\ -k_3\cdot y_2 + k_2\cdot M\cdot y_0\cdot y_1 - k_4\cdot y_0\cdot y_2 \end{bmatrix}$$

$$J(t,y) := \begin{bmatrix} 0 & -k_2\cdot M\cdot y_1 - k_4\cdot y_2 & 2\cdot k_1 - k_2\cdot M\cdot y_0 & k_3 - k_4\cdot y_0 \\ 0 & -k_2\cdot M\cdot y_1 + 2\cdot k_4\cdot y_2 & -k_1 - k_2\cdot M\cdot y_0 & k_3 + 2\cdot k_4\cdot y_0 \\ 0 & k_2\cdot M\cdot y_1 - k_4\cdot y_2 & k_2\cdot M\cdot y_0 & -k_3 - k_4\cdot y_0 \end{bmatrix}$$

$\text{answers} := \text{Stiffr}(y, 0, \text{tmax}, \text{npts}, D, J)$

$t := \text{answers}^{<0>}$

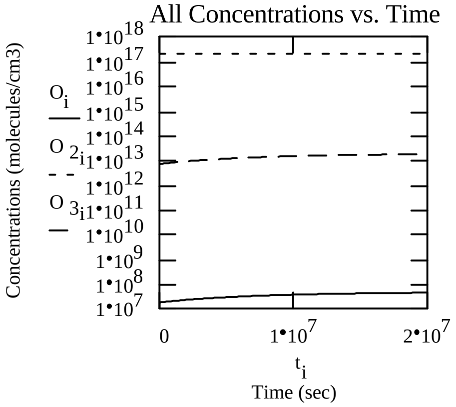
$O := \text{answers}^{<1>}$

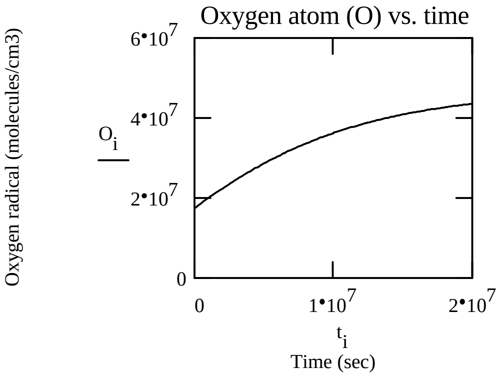
$O_2 := \text{answers}^{<2>}$

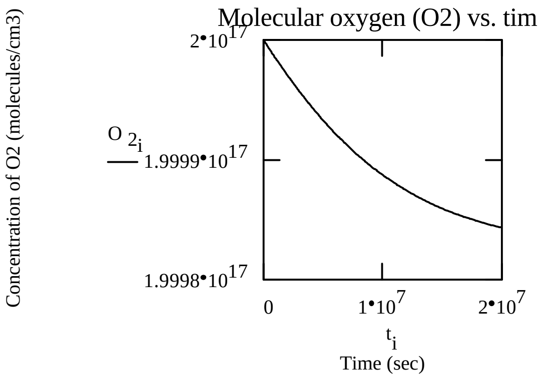
$O_3 := \text{answers}^{<3>}$

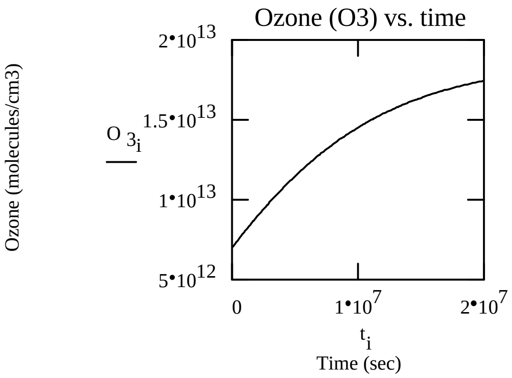
The temperature can be changed right here, for convenience. Be sure to use the Kelvin units.

$T \equiv 220\cdot K$









Exercises:

12. Within the stratosphere, the temperature varies from 215 K to 270 K. How significant is the effect that such variations in the temperature have on the model results?

13. Try using a sinusoidal function in place of the constants k_1 and k_3, to model the actual effects of sunlight as it goes through daily and/or yearly intensity fluctuations. You will need to alter the D and J matrices to reflect the sinusoidal natures of k_1 and k_3.

Answers to Selected Exercises:

Exercise 1. Why is a third body not needed in Step 4?

The energy released during the Step 4 reaction can be divided between two product molecules, rather than being dumped into a single product molecule.

Exercise 2. The reactions above represent a chain reaction. Identify the initiation, propagation and termination steps.

Initiation:	Step 1	O_2 ---> 2 O
Propagation:	Step 2	M + O + O_2 ---> M + O_3
	Step 3	O_3 ---> O + O_2
Termination:	Step 4	O + O_3 ---> 2 O_2

Exercise 3. Add together the two chain propagation steps. What is the overall reaction?

There is no net overall reaction - all of the species cancel out! The significance of this pair of propagation reactions is that photons are absorbed to drive Step 3, and then the corresponding release of energy in Step 2 is stored as increased kinetic energy of M and O_3.

Exercise 4. What are the units of concentration being used? Why would these units be chosen rather than molarity?

The units of concentration are molecules/cm^3. These units are useful for the very low concentrations exhibited by trace atmospheric species. (1 mole/liter = 6.02 x 10^{20} molecules/cm^3)

Exercise 5. Explain how the cycle of reactions operates to warm the stratosphere. Which two reactions are most important for the warming effect? Why

Steps 2 and 3, the propagation steps discussed in Exercise 3, are the most important warming steps simply because they occur over and over. The ultraviolet light absorbed in Step 3 is released as heat in Step 2 (increased kinetic energy of the molecules involved.) While Step 4 releases a great deal of energy (more than Step 2), it does not occur as often as the propagation steps.

Exercise 6:

Stop and write out the differential rate equations for the other two constituents now.

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

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

The differential equations describing formation and loss of each species are shown here.

$$\frac{d}{dt}O_3 = -k_3\cdot O_3 + k_2\cdot M\cdot O\cdot O_2 - k_4\cdot O\cdot O_3$$

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References:

1. "*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.

2. Noggle, Joseph, "*Physical Chemistry Using Mathcad,*" Pile Creek Publishing Company: Newark, Delaware, 1997 p.211.

Other ozone-related resources:

3. Matthew Elrod's web site at Hope College provides links to environmental chemistry sites with information about stratospheric ozone chemistry. He has also written several Mathcad documents that model tropospheric and stratospheric ozone kinetics and provide useful insights about the results. His home page is

http://www.chem.hope.edu/~elrod

and the same address plus

/mathcad/chapkey.mcd
/mathcad/chap+noxkey.mcd
/smogkey.mcd

points to the mathcad documents.

4. An ozone chemistry teaching resource directed at the general chemistry level was developed through the ChemLinks Coalition based at Beloit College and funded by NSF's systemic change initiative in chemistry. The reference is T. Ferrett and S. Anthony, "Why does the ozone hole form?" Wiley and Sons, Inc., ChemConnections module, "Beta" version published Fall, 1998. To use the module, contact Heather Mernitz at Beloit College (Mernitzh@Beloit.edu) or Brock Spencer, the ChemLinks Project Director (Spencer@Beloit.edu). For more information on ChemLinks, see http://chemlinks.beloit.edu.