The Kinetics of Atmospheric Ozone

Ozone is a minor component of the earth's atmosphere (0.02 – 0.1 parts per million based on volume (ppm_v)), yet it has a significant role in sustaining life on earth. It absorbs ultraviolet (uv) radiation from the sun and hence reduces the levels of uv radiation reaching the earth's surface . UV radiation, being of short wavelength and hence highly energetic, can cause damage to plant and animal life on earth. Measurements of the levels of ozone in the atmosphere indicate that ozone levels have been dropping, with significant decreases since the 1970's. This drop in ozone levels seems to coincide with increases in cases of skin cancer, and eye cataracts in humans, and DNA damage to plant and marine life. Due to its environmental significance, the chemistry of atmospheric ozone and ozone depletion has been a subject of much research and discussion. In fact, the 1995 Nobel Prize in Chemistry was awarded to three scientists who revealed the role of "man-made" chemicals, chlorofluorocarbons, or CFC's, in the ozone depletion process.

This exercise investigates the kinetics of ozone formation and depletion in the atmosphere. First you will use Excel to determine the concentration profile of ozone in the atmosphere. Next, you will use a mathematical program called "Mathematica" to investigate the kinetics of ozone reactions in the atmosphere.

Chapman mechanism

The original mechanism for atmospheric ozone formation and destruction from oxygen species was suggested by Chapman in 1930. The elementary reactions which constitute the Chapman mechanism are:

$O_2 + h\nu \rightarrow 2\ O$ $\quad k_1\ (s^{-1})$ $\quad$ (1)

$O + O_2 + M \rightarrow O_3 + M$ $\quad k_2\ (cm^6\ molecule^{-2}\ s^{-1})$ $\quad$ (2)

$O_3 + h\nu \rightarrow O + O_2$ $\quad k_3\ (s^{-1})$ $\quad$ (3)

$O + O_3 \rightarrow 2\ O_2$ $\quad k_4\ (cm^3\ molecules^{-1}\ s^{-1})$ $\quad$ (4)

M is any non-reactive species that can take up the energy released in reaction (2) to stabilize O_3. O_3 is not a very stable molecule and (without the presence of M) the O_3 formed by the collision of O_2 and O would immediately fall apart to give back O and O_2. Given that N_2 and O_2 are the major components in the atmosphere, M is either O_2 or N_2.

The rate constants k_1 and k_3 depend on light intensity, which in this case is the light intensity of the sun.

Order of the Reactions

Looking at each elementary reaction, we would expect that reaction (1) follows first order kinetics, reaction (2) follows third order kinetics, reaction (3) follows first order kinetics and reaction (4) follows second order kinetics. Note that reaction (2) requires three species to come together at the same time, i.e. it is a termolecular reaction. If we look at the relative concentration of species in the atmosphere, O_2 and M (= O_2 + N_2) have much higher concentrations than O and O_3, and so they can be considered to be essentially constant over time. Thus, we might expect reaction (1) to obey zero order kinetics (a “pseudo” zero order reaction) and reaction (2) to obey first order kinetics (“pseudo” first order reaction).

Rate of formation of O and O_3

The concentration of ozone is found to be higher in the upper atmosphere (the stratosphere) when compared with the concentrations in the lower atmosphere (the troposphere). From reactions (1) to (4) the rates of formation of O and O_3 can be expressed as:

$$\frac{d[O]}{dt} = 2k_1[O_2] - k_2[O][O_2][M] + k_3[O_3] - k_4[O][O_3] \qquad (5)$$

$$\frac{d[O_3]}{dt} = k_2[O][O_2][M] - k_3[O_3] - k_4[O][O_3] \qquad (6)$$

We can use the steady-state approximation to solve for the concentration of O and O_3. The steady state approximation assumes that after an initial time period, the concentration of the reaction intermediates remain a constant with time, i.e the rate of change of the intermediate’s concentration with time is zero. Hence, using the steady state approximation

$$\frac{d[O]}{dt} = \frac{d[O_3]}{dt} = 0 \qquad (7)$$

we can solve for [O] and $[O_3]$

$$[O] = \frac{2k_1[O_2] + k_3[O_3]}{k_2[O_2][M] + k_4[O_3]} \qquad (8)$$

$$[O_3] = \frac{k_2[O][O_2][M]}{k_3 + k_4[O]} \tag{9}$$

Equation (9) can be rearranged:

$$[O_3] = \frac{k_2[O_2][M]/k_4}{[k_3/(k_4[O])] + 1} \tag{10}$$

The reactions (1) to (4) have been very well studied and the rate constants for these reactions at different altitudes are known. For example, $k_1 \sim 10^{-12}$ s^{-1}, $k_2 \sim 2x10^{-33}$ cm^6 $molecule^{-2}s^{-1}$, $k_3 \sim 10^{-3}$ s^{-1}, $k_4 \sim 10^{-15}$ cm^3 $molecule^{-1}s^{-1}$. In addition, the concentrations of O, O_2 and O_3 in the atmosphere are known. If we assume that $[O] \sim 10^7$ molecule/cm^3 and $[O_3] \sim 10^{13}$ molecule/cm^3, using the values of the rate constants above we find that

$$\frac{k_3}{k_4[O]} >> 1$$

Hence equation (10) can be simplified to

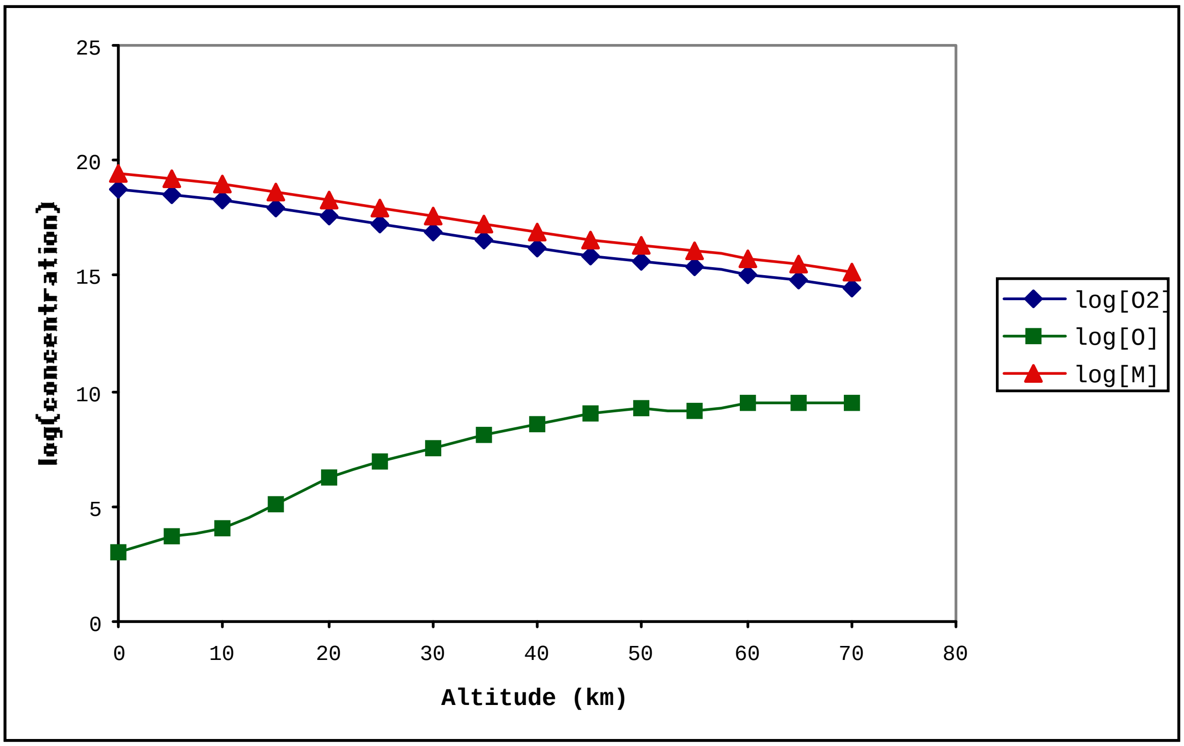
$$[O_3] \approx \frac{k_2[O_2][M][O]}{k_3} \tag{11}$$

Equation 11 indicates that the concentration of O_3 in the atmosphere depends proportionately on the rate of reaction 2 and inversely on k_3, the rate constant for the photolysis of ozone by the uv light from the sun .

Variation of Ozone Concentration with Altitude

Measurements indicate that the concentration of ozone increases with altitude and so the concentration of ozone is higher in the upper atmosphere, the stratosphere, than in the lower atmosphere, the troposphere. This is good for life on earth since this means that the harmful uv radiation is strongly attenuated by ozone absorption far from the earth's surface.

To understand the concentration profile of O_3 as a function of altitude open the Excel file "ozone.xls". In this file you will see entries for the concentration of O, O_2 and M as a function of altitude. These three species are the "ingredients" for ozone formation (see reactions 1 & 2). To graphically view the variation of the concentration of these three species as a function of altitude you will create a plot of the log of the concentration of each species versus altitude. So, first calculate the log of the concentration of each species. Select the appropriate columns and create an XY scatter plot of log(concentration) versus altitude with lines connecting each data point for each chemical species. You should see a log plot of the variation of each species as a function of altitude that looks like the plot below. Note the trend for each species. Also, note that this is a LOG plot and hence a change of 1 log unit corresponds to a factor of 10 change in concentration.



Now, using equation 11, calculate the concentration of O_3 as a function of altitude and, by selecting the appropriate columns, create an XY scatter plot ($[O_3]$ vs altitude)with a line connecting the points.

QUESTIONS

1) Note the variation of concentration of O, O_2 and M with increasing altitude. Why do you think the concentration of O increases with altitude?
2) Comment on how the concentration of ozone varies with altitude. Can you explain the trend?
2) Based on the two plots and your answers to questions (1) & (2), which species determines the concentration profile of O_3 as a function of altitude?
4) Explain why the rate of formation of O_3 behaves as a pseudo first order reaction.

Evaluation of the Rate Equations

We will now look at how sensitive the Chapman mechanism is to the rate constants of the elementary reactions. To do this we will use a program called "Mathematica" to solve the rate equations for the ozone reactions in the atmosphere and plot the results. Note that this approach allows us to "abandon" the steady state approximation in favor of direct numerical solutions to the differential equations that describe the elementary kinetic steps. Since the programming language of Mathematica is not "obvious", the equations have been programmed for you. All you will have to do is make changes to certain parameters and see how these parameters affect the rate of ozone formation in the atmosphere.

The rate of formation of O and O_3 are expressed in equations (5) and (6). We will assume that the oxygen concentration is a constant. Hence,

$$\frac{d[O_2]}{dt} = 0 \qquad (12)$$

(Note that this assumption flows from the large size of $[O_2]$ and not from a competition between creating and removing a species as is the case when we use the steady state approximation.) Equations (5) and (6) are coupled differential equations that are not trivial to solve. Mathematica will solve these equations using numerical algorithms for solving differential equations. We will have to provide the rate constants, the initial concentrations of O, O_2 (constant), and O_3 and the time period over which we would like to evaluate the equations. Mathematica will graph the rate of formation of O_3 over the given time period. You will then be able to vary the rate constants and see how sensitive the rate of formation of ozone is to these values.

Open the Mathetmatica file called "ozone2000.nb". You will see some text in blue – these are comments to explain the lines of programming that follow (any lines beginning with (*

and ending with *) are comment lines). The black text are the lines of programming that are evaluated by Mathematica. The red lines denote the input that Mathematica uses for its calculations. You will be asked to change some of the red input lines to see how these values affect the rate of ozone formation.

Look at the red lines. First, the rate constants for each of the above reactions are listed; note the units of each rate constant. Following this list is the initial concentration of each species in units of molecules/cm^3 (at an altitude of 30 km) The last set of red lines indicate the time period over which the rate equations will be evaluated; the equations will be evaluated from t_1 = 0 to t_2= 42 days. (Note that we have changed the time to days to make the plot more convenient.)

Select the entire block of code by clicking the Mathematica page all the way at the right. You will note that the cursor changes to |← which indicates that this is the block of code to be submitted for evaluation. On selecting this block hit the "ENTER" key on the numeric key pad all the way to the right of the keyboard (or shift-ENTER on the regular keyboard). Mathematica will now evaluate equations (5) and (6) for the given input values. You will see a plot come up on the screen which is the rate of ozone formation (at an altitude of 30 km). Note the shape of the curve. Under these input conditions it takes over 42 days for the ozone concentration to reach its equilibrium value.

To see how sensitive the rate of formation of ozone is to the rate constants of each step you can change the value of the rate constant for one of the steps and re-evaluate the block of code. The plot will be automatically refreshed to reflect the change. For example, try increasing or decreasing k_2 by a factor of 10 by selecting 5.6 and typing 56 or 0.56. On making the change, select the block of code on the right, and hit the Enter key. Note how the rate of formation of ozone changes with changes in k_2. You can make similar changes to the other rate constants or initial concentrations of the reactants.

QUESTIONS

1) The formation and destruction of ozone depends on light intensity. To see this, raise k_1 and k_3 by a factor of 10, which corresponds to higher light intensity, and see how this affects the rate of formation of ozone. Conversely, lower k_1 and k_3 by a factor of 10 and

see how this affects the rate of formation of ozone. (If necessary, change the value of t_2). Based on your observations, comment on how ozone production varies over a day. How does the level of uv light reaching the earth's surface vary over a day?

2) Would you expect the production of ozone to be higher over the equator or over the poles? Explain your choice of answer.
3) In the model we employed to carry out this calculation, we assumed constant light intensity over a period of 42 days. In a more realistic picture, we should account for the difference in light intensity between day and night. During the night, the rate constants of reactions 1 and 3 can be estimated to be 100 times smaller than those during the day. To see how this adjustment affects ozone concentration over time, solve the differential equations 5 and 6 for alternating periods of high and low light intensity. You can assume that day and night are each 12 hours long. As initial conditions of each 12 hour period, you should use the final concentrations of the previous twelve hour period.

   Create a new notebook (File → New) and copy into it the contents of ozone2002. nb. Use the syntax from this file to calculate and plot ozone concentration versus time in 12 hour intervals over a period of 5 days. Sketch your results on one graph. PAY ATTENTION TO THE SCALE ON THE Y AXIS! For each 12 hour period, remember to:

(a) adjust k_1 and k_3 (make each 100 times smaller for night hours)
(b) use final concentrations of the previous period as the initial conditions. Use

   B[time in days] /. solution

   C[time in days] /. solution

   (the last two lines of code) to get the concentrations of O atoms and ozone at the end of the interval.
(c) keep the time interval as t1 = 0 and t2 = 0.5 days.
(d) How do the values of ozone concentration after 5 days differ in the model where the light is assumed to be on continuously versus the model where the light is shut off at night?

Competing Reactions to the Chapman mechanism.

Estimates of the ozone concentration based on the Chapman mechanism turn out to be higher than the measured concentration of ozone. Hence, there must be other reactions occurring in the stratosphere that lower the ozone concentration below that predicted by reactions (1) to (4). Experiments and measurements indicate that there are other atmospheric species which react with O_3. Some of these species are "natural", in that they are produced by natural phenomena, others are due to "man-made" chemicals released in the atmosphere. In the last exercise, we will look at how one family of man-made compounds couples with the Chapman mechanism, affecting the concentration of ozone in the atmosphere. The family of compounds we will look at is the chlorofluorocarbons, or CFC's.

CFC's are chlorine and fluorine containing hydrocarbons that were used as refrigerants, electronic cleaners, etc. A common CFC is Freon 12, CF_2Cl_2. In the atmosphere CF_2Cl_2 undergoes the following reaction;

$$CF_2Cl_2 + h\nu \rightarrow CF_2Cl + Cl \qquad k_5 = 1.0 \times 10^{-7}\ s^{-1} \tag{13}$$

The Cl then reacts with O_3:

$$Cl + O_3 \rightarrow ClO + O_2 \qquad k_6 = 2.1 \times 10^{-11}\ cm^3\ molecule^{-1} s^{-1} \tag{14}$$

$$ClO + O \rightarrow Cl + O_2 \qquad k_7 = 3.8 \times 10^{-11}\ cm^3\ molecule^{-1} s^{-1} \tag{15}$$

How does this set of reactions affect the rate of formation of ozone? We have to "add" these three reactions to reactions (1) to (4) and solve the rate equations for d[O]/dt, d[O_3]/dt, d[Cl]/dt, d[ClO]/dt.

$$\frac{d[O]}{dt} = 2k_1[O_2] - k_2[O][O_2][M] + k_3[O_3] - k_4[O][O_3] - k_7[ClO][O] \tag{16}$$

$$\frac{d[O_3]}{dt} = k_2[O][O_2][M] - k_3[O_3] - k_4[O][O_3] - k_6[Cl][O_3] \tag{17}$$

$$\frac{d[CF_2Cl_2]}{dt} = -k_5[CF_2Cl_2] \tag{18}$$

$$\frac{d[Cl]}{dt} = k_5[CF_2Cl_2] - k_6[Cl][O_3] + k_7[ClO][O] \tag{19}$$

$$\frac{d[ClO]}{dt} = k_6[Cl][O_3] - k_7[ClO][O] \tag{20}$$

Open the Mathematica file “ozone_CFC2002.nb”. This file will solve the coupled differential equations (16) to (20). Select the block of code and execute it (using either shift-Enter or Enter on the number pad).

QUESTIONS

1) Comment on how the concentration of ozone is affected by the presence of CFC’s. Comment on the time period over which the CFC computation is made compared to the Chapman mechanism computation.

2) Based on your observations, why do you think CFC usage has been banned?