1. The Chapman mechanism and steady state

We compare here some features of the Chapman mechanism at 20 km and 45 km altitude. Adopt temperatures of 200 K at 20 km altitude and 270 K at 45 km altitude, and air densities of 1.8×10^{18} molecules cm^{-3} at 20 km altitude and 4.1×10^{16} molecules cm^{-3} at 45 km altitude. The reactions in the Chapman mechanism are

$O_2 + h\nu \rightarrow O + O$ (1)
$O + O_2 + M \rightarrow O_3 + M$ (2)
$O_3 + h\nu \rightarrow O_2 + O$ (3)
$O_3 + O \rightarrow 2O_2$ (4)

with rate constants $k_2 = 1\times10^{-33}$ cm^6 molecule^{-2} s^{-1}, $k_3 = 1\times10^{-2}$ s^{-1}, and $k_4 = 8.0\times10^{-12}\exp(-2060/T)$ cm^3 molecule^{-1} s^{-1} where T is temperature.

1.1. Calculate the lifetime of the O atom at 20 km and 45 km altitude. Can the O atom be assumed in chemical steady state throughout the stratosphere?

1.2. Assuming steady state for O atoms, calculate the O/O_3 concentration ratio at 20 km and 45 km altitude. Can we assume $[O_3] \cong [O_x]$ throughout the stratosphere?

1.3. Show that the mass balance equation for odd oxygen ($O_x = O_3 + O$), ignoring transport terms, can be written

$$\frac{d[O_x]}{dt} = P - k[O_x]^2$$

where $P = 2k_1[O_2]$ is the O_x production rate and $k = 2k_3k_4/(k_2C_{O_2}n_a^2)$. ($n_a$ is the air number density).

1.4. Express the lifetime of O_x as a function of k and $[O_x]$.

2. Effects of the solar cycle

The solar UV radiation varies by a few percent over the 11-year solar cycle, and the stratospheric O_3 is expected to respond to such solar forcing. Its effect is mainly in the spectrum where O_2 absorbs.

2.1. Use your O_x equation derived from the previous quesiton to calculate the relative change in O_3 density for a 2% decrease in JO_2. Justify your steady state assumption. (Hint: You may need to consult your calculus book on derivative.)

2.2. As O_3 change, temperature in the stratosphere also changes. The change in heating rate due to O_3 absorption of UV radiation is estimated at $\Delta H = a\Delta[O_3]/[O_3]$ and the change in cooling rate due to O_3 IR emission is estimated at $\Delta C = b\Delta T$, with $a/b = 0.1$. Estimate the change of temperature due to the decrease of O_3.

3. Chlorine chemistry at mid-latitudes

An air parcel at 30 km altitude (30°N, equinox) contains the following concentrations:

$[O_3] = 3.0\text{x}10^{12}$ molecules cm^{-3}

$[O] = 3.0\text{x}10^{7}$ atoms cm^{-3}

$[NO] = 7\text{x}10^{8}$ molecules cm^{-3}

$[NO_2] = 2.2\text{x}10^{9}$ molecules cm^{-3}

$[HO_2] = 8.5\text{x}10^{6}$ molecules cm^{-3}

$[CH_4] = 2.8\text{x}10^{11}$ molecules cm^{-3}

We examine the mechanism for Cl-catalyzed O_3 loss in this air parcel on the basis of the following reactions:

$Cl + O_3 \rightarrow ClO + O_2$	$k_1 = 9.5\text{x}10^{-12}$ cm^3 molecule^{-1} s^{-1} (1)
$Cl + CH_4 \rightarrow HCl + CH_3$	$k_2 = 2.6\text{x}10^{-14}$ cm^3 molecule^{-1} s^{-1} (2)
$ClO + O \rightarrow Cl + O_2$	$k_3 = 3.8\text{x}10^{-11}$ cm^3 molecule^{-1} s^{-1} (3)
$NO_2 + h\nu \rightarrow NO + O$	$k_4 = 5.0\text{x}10^{-3}$ s^{-1} (4)
$ClO + NO \rightarrow Cl + NO_2$	$k_5 = 4.5\text{x}10^{-11}$ cm^3 molecule^{-1} s^{-1} (5)
$ClO + HO_2 \rightarrow HOCl + O_2$	$k_6 = 2.1\text{x}10^{-11}$ cm^3 molecule^{-1} s^{-1} (6)
$ClO + NO_2 + M \rightarrow ClNO_3 + M$	$k_7 = 1.3\text{x}10^{-13}$ cm^3 molecule^{-1} s^{-1} (7)
$HOCl + h\nu \rightarrow OH + Cl$	$k_8 = 2.5\text{x}10^{-4}$ s^{-1} (8)
$OH + O_3 \rightarrow HO_2 + O_2$	$k_9 = 2.8\text{x}10^{-14}$ cm^3 molecule^{-1} s^{-1} (9)

3.1. Calculate the chemical lifetimes of Cl and ClO. Which reaction is the principal sink for each?

3.2. Based on your answer to question 1, explain why reaction (3) is the rate-limiting step in the catalytic cycle for O_3 loss:

$Cl + O_3 \rightarrow ClO + O_2$ (1)
$ClO + O \rightarrow Cl + O_2$ (3)

3.3. In question 2, if ClO reacts with NO instead of with O, do you still get a catalytic cycle for O_3 loss? Briefly explain.

3.4. Write a catalytic cycle for O_3 loss involving the formation of HOCl by reaction (6). How does this mechanism compare in importance to the one in question 2?

3.5. Calculate the lifetime of the chemical family ClO_x defined as the sum of Cl and ClO. Compare to the lifetime of ClO. What do you conclude?

4. OH concentrations in the past

There has been interest in using Greenland ice core measurements of methane (CH_4) and formaldehyde (CH_2O) to derive OH concentrations in the past.

(1) The main sink for CH_2O in the Arctic is photolysis, with a mean rate constant $k = 1x10^{-5}\ s^{-1}$. Oxidation of CH_4 is the only significant source of CH_2O. Show that the steady-state concentration of CH_2O is given by

$$[CH_2O] = \frac{k'}{k}[CH_4][OH]$$

where $k' = 2.0x10^{-12} \exp(-1700/T)\ cm^3\ molecule^{-1}\ s^{-1}$ is the rate constant for oxidation of methane by OH.

(2) The Table below shows the concentrations (ppbv) of CH_2O and CH_4 in Greenland for three historical periods: present, pre-industrial (1600 A.D.), and last glaciation (18,000 B.C.).

	[CH_4]	**[CH_2O]**	**T, K**
Present	1700	0.10	260
Preindustrial	740	0.050	260
Glacial	410	0.010	250

(2.1) Compute the OH concentration (molecules cm^{-3}) over Greenland for each period.

(2.2) How do you interpret the difference in OH concentrations between pre-industrial times and today?

(2.3) One possible explanation for the difference in OH concentrations between glacial and pre-industrial times is that stratospheric ozone concentrations were higher in glacial times. Why would that be? How would that affect OH concentrations?

5. Sources of tropospheric ozone

(1) Ozone is supplied to the troposphere by transport from the stratosphere. We estimate here the magnitude of this source by using the two-box model for stratosphere-troposphere exchange, where $k_{ST} = 0.7\ yr^{-1}$ is the transfer rate constant of air from the stratosphere to the troposphere and $k_{TS} = 0.14\ yr^{-1}$ is the reverse transfer rate constant from the troposphere to the stratosphere. Observations indicate that the atmosphere

contains 5×10^{13} moles of O_3 and that 90% of that total is in the stratosphere (the remaining 10% is in the troposphere). Calculate the net source of tropospheric O_3 contributed by transport from the stratosphere.

(2) Ozone is also produced within the troposphere by oxidation of CO and hydrocarbons (principally CH_4) in the presence of NO_x. One of the earliest estimates of the global source of ozone in the troposphere was done by scaling the emission inventories of CH_4 and CO. We repeat this calculation here. Consider the following mechanism for oxidation of CH_4 and CO to CO_2 under high-NO_x conditions:

$$CH_4 + OH \xrightarrow{O_2} CH_3O_2 + H_2O$$

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2$$

$$CH_3O + O_2 \rightarrow CH_2O + HO_2$$

$$NO_2 + h\nu \xrightarrow{O_2} NO + O_3$$

$$HO_2 + NO \rightarrow OH + NO_2$$

$$CH_2O + OH \rightarrow CHO + H_2O$$

$$CHO + O_2 \rightarrow CO + HO_2$$

$$CO + OH \xrightarrow{O_2} CO_2 + HO_2$$

(2.1) Write a net reaction for the oxidation of CO to CO_2 by the above mechanism. Do the same for the oxidation of CH_4 to CO_2 (some of the reactions may proceed more than once). How many O_3 molecules are produced per molecule of CO oxidized? per molecule of CH_4 oxidized?

(2.2) Present-day global emission estimates are 3×10^{13} moles yr^{-1} for CH_4 and 4×10^{13} moles yr^{-1} for CO. Using your results from question (2.1), estimate the global production rate of ozone in the troposphere.

(2.3) The range of estimates for the global chemical production rate of ozone in the troposphere, as derived from 3-dimensional models of tropospheric chemistry, is 6-10×10^{13} moles yr^{-1}. Explain how the approach you used in question (2.2) might be expected to overestimate the production rate of ozone.