

## PROBLEMS

### 10. 1 Shape of the ozone layer

Consider a beam of solar radiation of wavelength  $\lambda$  propagating downward in the vertical direction with an actinic flux  $I_\infty$  at the top of the atmosphere. Assume that  $O_2$  is the sole atmospheric absorber of this radiation.

1. Show that the  $O_2$  photolysis rate  $R$  from this radiation beam varies with altitude  $z$  as follows:

$$R(z) = q\sigma C_{O_2} n_a(0) I_\infty \exp\left[-\frac{z}{H} - \sigma C_{O_2} H n_a(z)\right]$$

where  $\sigma$  is the absorption cross-section for  $O_2$  at wavelength  $\lambda$ ,  $q$  is the corresponding quantum yield for  $O_2$  photolysis,  $n_a(z)$  is the air density,  $H$  is the scale height of the atmosphere, and  $C_{O_2}$  is the  $O_2$  mole fraction.

2. Sketch a plot of  $R$  vs.  $z$ . Comment on the shape. Explain physically why  $R(z)$  has a maximum in the atmospheric column.

### 10. 2 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  $1.8 \times 10^{18}$  molecules  $\text{cm}^{-3}$  at 20 km altitude and  $4.1 \times 10^{16}$  molecules  $\text{cm}^{-3}$  at 45 km altitude. The reactions in the Chapman mechanism are



with rate constants  $k_2 = 1 \times 10^{-33} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ ,  $k_3 = 1 \times 10^{-2} \text{ s}^{-1}$ , and  $k_4 = 8.0 \times 10^{-12} \exp(-2060/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  where  $T$  is temperature.

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?

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

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

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

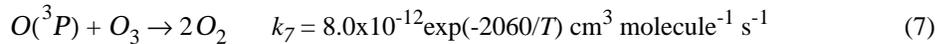
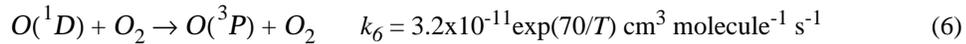
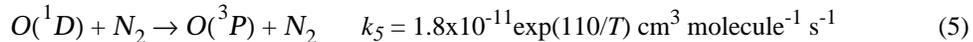
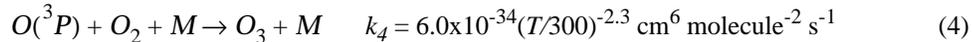
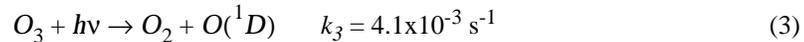
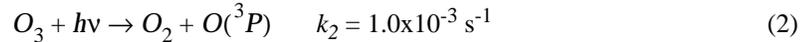
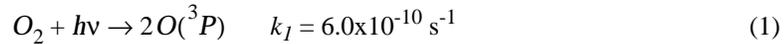
where  $P = 2k_1[O_2]$  is the  $O_x$  production rate and  $k = 2k_3k_4/(k_2C_{O_2}n_a^2)$ .

4. Express the lifetime of  $O_x$  as a function of  $k$  and  $[O_x]$ . Using the vertical distribution of  $O_3$  at the equator in Figure 10-1, calculate the lifetime of  $O_x$  at 20 km and 45 km altitude.

5. Based on your answer to question 4, in what part of the stratosphere would you expect  $O_x$  to be in chemical steady state? How would that help you test the accuracy of the Chapman mechanism in predicting ozone levels?

### 10.3 The detailed Chapman mechanism

We examine here some features of the detailed Chapman mechanism. Consider an air parcel at 44 km altitude, 30°N latitude, overhead Sun,  $T = 263$  K,  $n_a = 5.0 \times 10^{16}$  molecules  $\text{cm}^{-3}$ , and  $[O_3] = 2.0 \times 10^{11}$  molecules  $\text{cm}^{-3}$ . The reactions involved in the mechanism are:



1. Assuming that reactions (1)-(7) are the only ones occurring in the air parcel:

1.1 Calculate the lifetime of  $O(^1D)$  in the air parcel and its steady-state concentration.

1.2 Calculate the lifetime of  $O(^3P)$  in the air parcel and its steady-state concentration.

1.3 Calculate the lifetime of  $O_x$  due to loss by the Chapman mechanism.

2. Assuming steady state for  $O_x$ , calculate the fraction of the total  $O_x$  sink in the air parcel that can actually be accounted for by the Chapman mechanism.

### 10.4 HO<sub>x</sub>-catalyzed ozone loss

Cycling of the HO<sub>x</sub> chemical family (HO<sub>x</sub> ≡ H + OH + HO<sub>2</sub>) can catalyze O<sub>3</sub> loss in a number of ways. Consider the following reactions, each important in at least some region of the stratosphere:



1. Find five different catalytic O<sub>3</sub> loss cycles starting with reaction of OH.
2. Which of the reactions represent sinks for HO<sub>x</sub>?

### 10.5 Chlorine chemistry at mid-latitudes

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

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

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

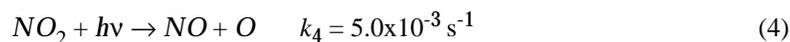
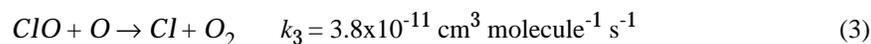
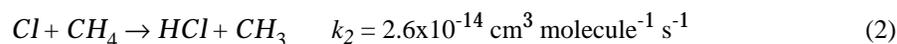
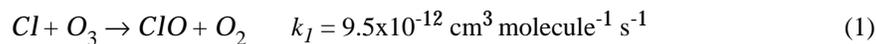
$$[NO] = 7 \times 10^8 \text{ molecules cm}^{-3}$$

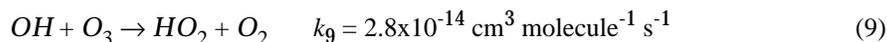
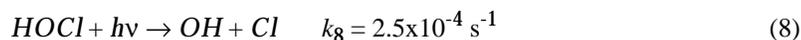
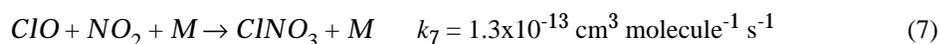
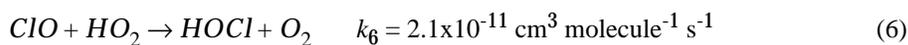
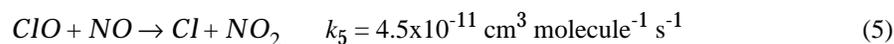
$$[NO_2] = 2.2 \times 10^9 \text{ molecules cm}^{-3}$$

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

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

We examine the mechanism for Cl-catalyzed O<sub>3</sub> loss in this air parcel on the basis of the following reactions:





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

2. Based on your answer to question 1, explain why reaction (3) is the rate-limiting step in the catalytic cycle for O<sub>3</sub> loss:



3. In question 2, if ClO reacts with NO instead of with O, do you still get a catalytic cycle for O<sub>3</sub> loss? Briefly explain.

4. Write a catalytic cycle for O<sub>3</sub> loss involving the formation of HOCl by reaction (6). How does this mechanism compare in importance to the one in question 2?

5. Calculate the lifetime of the chemical family ClO<sub>x</sub> defined as the sum of Cl and ClO. Compare to the lifetime of ClO. What do you conclude?

[To know more: McElroy, M.B., et al., The changing stratosphere, *Planet Space Sci.*, 40, 373-401, 1992.]

## 10.6 Partitioning of Cl<sub>y</sub>

The POLARIS aircraft mission to the arctic in the summer of 1997 provided the first *in situ* simultaneous measurements of HCl and ClONO<sub>2</sub> in the lower stratosphere (20 km altitude). These data offer a test of current understanding of chlorine chemistry. According to current models, the principal Cl<sub>y</sub> cycling reactions operating under the POLARIS conditions should be





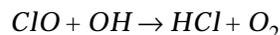
with rate constants  $k_1 = 8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,  $k_2 = 7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,  $k_3 = 1.3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,  $k_4 = 7 \times 10^{-5} \text{ s}^{-1}$ ,  $k_5 = 3 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , and  $k_6 = 5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Consider the following concentrations typical of the air sampled in POLARIS:  $[O_3] = 5 \times 10^{12} \text{ molecules cm}^{-3}$ ,  $[NO] = 4 \times 10^9 \text{ molecules cm}^{-3}$ ,  $[NO_2] = 1.5 \times 10^{10} \text{ molecules cm}^{-3}$ ,  $[CH_4] = 1.7 \times 10^{12} \text{ molecules cm}^{-3}$ , and  $[OH] = 2 \times 10^6 \text{ molecules cm}^{-3}$ .

1. Draw a diagram of the  $Cl_y$  cycle and calculate the lifetime of each  $Cl_y$  component.
2. Consider the chemical family  $Cl_z = Cl + ClO + ClNO_3$ . What is the main component of  $Cl_z$ ? What is the lifetime of  $Cl_z$ ?
3. Starting from an initial input of HCl to the stratosphere, show that the characteristic time for HCl to equilibrate with the other components of the  $Cl_y$  family is 5 days.
4. The characteristic time derived in question 3 is sufficiently short that HCl and  $ClNO_3$  should be near chemical steady state for the atmosphere sampled during POLARIS. Show that the steady-state  $[ClNO_3]/[HCl]$  ratio from reactions (1)-(8) is

$$\frac{[ClNO_3]}{[HCl]} = \frac{k_1 k_3 k_6 k_7 [O_3]^2 [OH]}{k_2 k_4 k_5 k_8 [CH_4]}$$

Explain qualitatively the quadratic dependence on the  $O_3$  concentration.

5. Observations in POLARIS indicate a  $[ClNO_3]/[HCl]$  ratio about 10% lower than calculated from the above equation. It has been proposed that the reaction

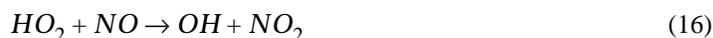


which until recently was not included in most models, could account for the discrepancy. Explain how. What would be the implication of this reaction for computed rates of  $ClO_x$ -catalyzed  $O_3$  loss?

## 10.7 Bromine-catalyzed ozone loss

Significant ozone loss can take place in the stratosphere by reactions involving inorganic bromine ( $Br_y = Br + BrO + HOBr + HBr + BrNO_3$ ) produced from the

degradation of methyl bromide (see problem 6. 4) and a number of industrial gases. Consider the following ensemble of reactions involved in the cycling of  $\text{Br}_y$ :



1. Draw a diagram of the  $\text{Br}_y$  cycle.
2. Identify three catalytic cycles for  $\text{O}_3$  loss involving bromine.

## 10. 8 Limitation of antarctic ozone depletion

High concentrations of chlorine radicals ( $\text{ClO}_x = \text{Cl} + \text{ClO}$ ) in the antarctic spring stratosphere cause rapid destruction of  $\text{O}_3$ . Recent observations indicate that the extent of  $\text{O}_3$  depletion in antarctic spring is ultimately limited by conversion of  $\text{ClO}_x$  to the long-lived  $\text{HCl}$  reservoir as  $\text{O}_3$  concentrations fall to very low levels. Consider an air parcel in the antarctic spring stratosphere containing 0.8 ppmv

$\text{CH}_4$ , 0.6 ppmv  $\text{O}_3$ , 0.3 ppbv  $\text{NO}_x$ , and 1.0 ppbv  $\text{ClO}_x$ , with an air density  $n_a = 3.5 \times 10^{18}$  molecules  $\text{cm}^{-3}$ . The following reactions cycle the  $\text{ClO}_x$  and  $\text{NO}_x$  radicals:



Rate constants are  $k_1 = 7.9 \times 10^{-12}$   $\text{cm}^3$  molecule $^{-1}$  s $^{-1}$ ,  $k_2 = 2.7 \times 10^{-11}$   $\text{cm}^3$  molecule $^{-1}$  s $^{-1}$ ,  $k_3 = 1.8 \times 10^{-15}$   $\text{cm}^3$  molecule $^{-1}$  s $^{-1}$ , and  $k_4 = 1 \times 10^{-2}$  s $^{-1}$ .

1. Assuming steady state for  $\text{ClO}_x$  and  $\text{NO}_x$  radicals, show that  $[\text{Cl}] \ll [\text{ClO}]$  and  $[\text{NO}] \ll [\text{NO}_2]$ .
2. What are the lifetimes of Cl and NO? Is the steady state assumption in question 1 realistic?
3. Conversion of  $\text{ClO}_x$  to HCl takes place by:



with rate constant  $k_5 = 1.0 \times 10^{-14}$   $\text{cm}^3$  molecule $^{-1}$  s $^{-1}$ . Show that the lifetime  $\tau$  of  $\text{ClO}_x$  against conversion to HCl is

$$\tau \approx \frac{k_1 [\text{O}_3] [\text{ClO}_x]}{k_4 k_5 [\text{NO}_x] [\text{CH}_4]}$$

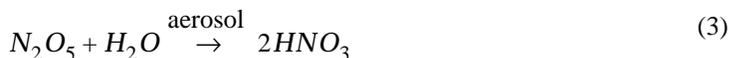
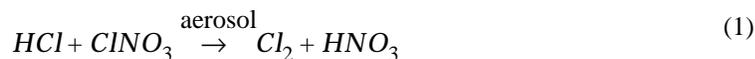
Calculate the numerical value of  $\tau$  as a function of the  $\text{O}_3$  concentration. Conclude regarding the eventual limitation of  $\text{O}_3$  depletion by reaction (5) in the antarctic stratosphere.

[Source: Mickley, L.J., et al., Evolution of chlorine and nitrogen species in the lower stratosphere during Antarctic spring: use of tracers to determine chemical change, *J. Geophys. Res.*, 102, 21,479-21,491, 1997]

## 10. 9 Fixing the ozone hole

Ozone depletion over Antarctica is catalyzed by chlorine radicals. An early theoretical study proposed that this depletion could be prevented by the injection of ethane ( $\text{C}_2\text{H}_6$ ) into the antarctic stratosphere. Ethane reacts quickly with Cl, converting it to HCl.

We examine here the effectiveness of this strategy. Consider the following ensemble of reactions taking place in the antarctic stratosphere:



Assume the following concentrations in the antarctic stratosphere when the polar vortex forms: HCl = 1.5 ppbv, ClNO<sub>3</sub> = 0.3 ppbv, and N<sub>2</sub>O<sub>5</sub> = 1.8 ppbv. Condensation of polar stratospheric clouds (PSCs) in the polar winter allows aerosol reactions (1)-(3) to proceed. Assume that all of the ClNO<sub>3</sub> reacts by reaction (1), that the excess HCl reacts by reaction (2), and that the leftover N<sub>2</sub>O<sub>5</sub> then reacts by (3). Both Cl<sub>2</sub> and ClNO<sub>2</sub> photolyze quickly (reactions 4 and 5) after the end of the polar night. The NO<sub>2</sub> formed by (5) reacts with ClO by reaction (7) to reform ClNO<sub>3</sub>.

1. Show that, after reactions (1)-(7) have taken place, the partitioning of chlorine is 0.6 ppbv (Cl+ClO), 1.2 ppbv ClNO<sub>3</sub>, and zero HCl.

2. The reaction of ethane with Cl is



If 1.8 ppbv ethane were injected into the polar stratosphere after reactions (1)-(7) have taken place, show that the partitioning of chlorine would shift to 1.2 ppbv (Cl+ClO), 0.6 ppbv HCl, and zero ClNO<sub>3</sub>. Would such an injection of ethane reduce O<sub>3</sub> loss?

3. How much ethane must actually be injected to convert all the chlorine present to HCl?

To know more: Cicerone, R.J., et al., Reduced Antarctic ozone depletions in a model with hydrocarbon injections, *Science*, 254, 1191-1194, 1991.]

### 10. 10 PSC formation

We examine here a few features of the  $\text{H}_2\text{O}$ - $\text{HNO}_3$  phase diagram relevant to PSC formation. Refer to Figure 10-12.

1. Is it possible for four phases to coexist at equilibrium in the  $\text{H}_2\text{O}$ - $\text{HNO}_3$  system? If so, under what conditions? Does the diagram show any regions or points with four coexisting phases?
2. Can NAT and  $\text{H}_2\text{O}$  ice particles coexist at equilibrium in the atmosphere? If so, up to what temperature?
3. Consider an air parcel initially containing  $\text{H}_2\text{O}$  and  $\text{HNO}_3$  with partial pressures  $P_{\text{H}_2\text{O}} = 1 \times 10^{-4}$  torr and  $P_{\text{HNO}_3} = 1 \times 10^{-6}$  torr. This air parcel cools rapidly during the polar night.
  - 3.1 At what temperature  $T_c$  do you expect PSC particles to form? What is the composition of these PSC particles?
  - 3.2 What happens as the temperature continues to fall below  $T_c$ ? Will a different type of PSC particle eventually be produced? [Hint: as the PSC particles condense,  $\text{H}_2\text{O}$  and/or  $\text{HNO}_3$  are gradually depleted from the gas phase according to the particle stoichiometry].