

# INTRODUCTION TO ATMOSPHERIC CHEMISTRY: SUPPLEMENTAL QUESTIONS AND PROBLEMS

5<sup>th</sup> EDITION

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## FOREWORD

The questions and problems presented here are intended to supplement my book *Introduction to Atmospheric Chemistry* (Princeton University Press, 1999). They are arranged following the different chapters of the book. In recent years I have added to my course lectures a chapter 14, ‘Aerosol Chemistry’ and a chapter 15, ‘Mercury in the Environment’. I have included here problems to support these chapters. All problems are from recent exams in my course.

This 5<sup>th</sup> edition includes a number of new problems and a few corrections to the previous (August 2011) edition.

The problems are aimed at the advanced undergraduate level. They try to tell interesting, realistic, and sometimes surprising stories, often addressing current research problems and drawing from recent literature. They all lend themselves to simple analytical solutions, with minimum computation. Although this limits the scope of the problems, I believe that it enhances their value for promoting understanding of processes. It also reveals the beauty of atmospheric chemistry, as the essence behind complicated real-world problems can often be found in simple relationships. I hope that you will find this as aesthetically pleasing as I do.

Complete solutions are available to instructors only. To obtain the solutions, send me an email certifying your instructor status. Reference to a university department website is generally sufficient.

Many thanks to Colette Heald (CSU), Randall Martin (Dalhousie), Gabriele Curci (U. L’Aquila), Amos Tai (Harvard), Jennifer Murphy (U. Toronto) for catching errors in previous editions. If you find any other errors or ambiguities please let me know. I very much hope that you will enjoy working through these problems and that you will find them interesting and useful.

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# CHAPTER 1: MEASURES OF ATMOSPHERIC COMPOSITION

## 1. Short questions

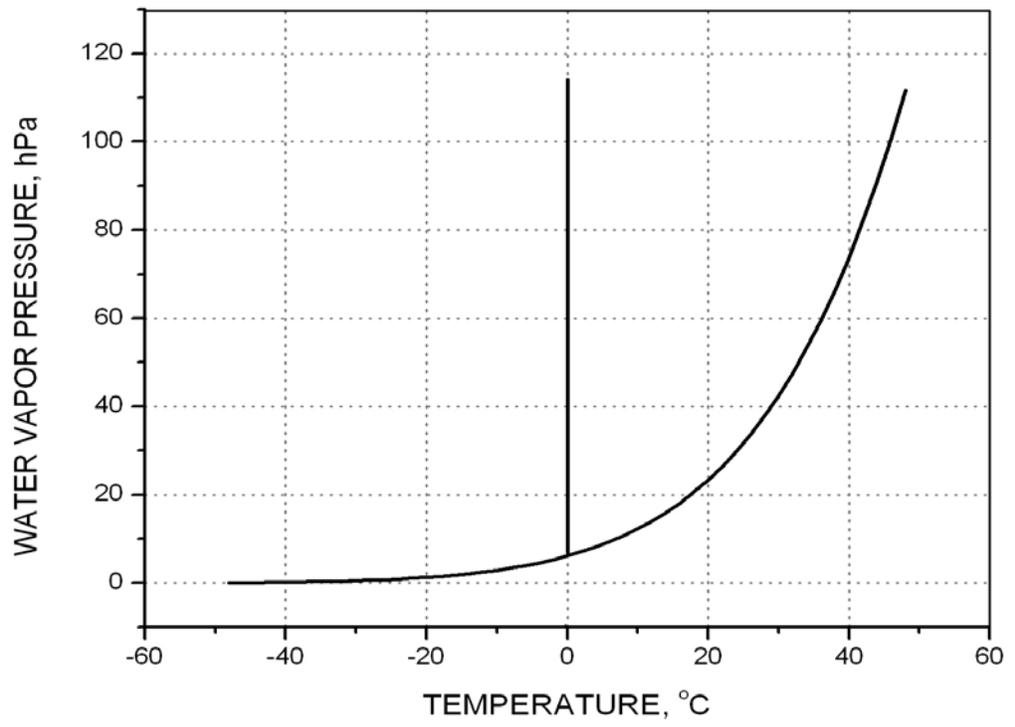
- 1.1 Oxygen has a fixed mixing ratio in the atmosphere. How would you expect its number density measured in surface air to vary between day and night? How would you expect its partial pressure measured in surface air to vary between day and night?
- 1.2 Give a rough order of magnitude for the number of molecules present in a typical 1 micrometer aerosol particle.
- 1.3 In an atmosphere with fixed mixing ratio of water vapor, what two processes can cause an increase in relative humidity?
- 1.4 We saw that a cloud in the atmosphere can remain liquid down to a temperature as low as 250 K. At a given temperature below freezing, and for a given total amount of water in an air parcel, will a cloud contain more condensed water if it is liquid or solid?
- 1.5 What is the fractional increase in mass of water-soluble aerosol particles when relative humidity increases from 90% to 95%? (assume that the aerosols are mainly water). Assuming that visibility degradation is proportional to the cross-sectional area of the particles, what is the resulting percentage decrease in visibility?

## 2. Seeing your breath

On cold mornings you can see your breath – let's figure out why. Consider the phase diagram of water below [Note that it looks different from the one in the book because it uses a linear scale for  $p_{H_2O}$ ]. Your breath is at 37°C and 90% relative humidity when it leaves your mouth (call this point A on the diagram). It mixes with outside air of a certain temperature and relative humidity (call this point B). Assuming that water vapor and heat are conserved during mixing, then the evolution of  $T$  and  $p_{H_2O}$  in the “breath plume” are given by

$$T = fT_B + (1 - f)T_A$$
$$p_{H_2O} = fp_{H_2O,B} + (1 - f)p_{H_2O,A}$$

where  $f$  varies from 0 at point A to 1 at point B. On the phase diagram, show the range of values for point B that would lead to cloud formation in the breath plume. Briefly explain and discuss your result.



## CHAPTER 2: ATMOSPHERIC PRESSURE

### 1. Short questions

- 1.1 A famous foot race in California starts from the bottom of Death Valley (100 m below sea level) and finishes at the top of Mt. Whitney (4300 m above sea level). This race is a challenge to the human organism! By what percentage does the oxygen number density decrease between the start and the finish of the race?
- 1.2 Why does it take longer to boil an egg in Denver than in Boston?

### 2. The Venusian atmosphere

Consider the following data for Venus and Earth:

	Radius, km	Surface pressure, atm	Mean atmospheric temperature, K	Atmospheric mixing ratios		
				CO <sub>2</sub>	N <sub>2</sub>	O <sub>2</sub>
Venus	6100	91	700	0.96	0.03	0.007
Earth	6400	1	250	0.0004	0.78	0.21

- 2.1 How does the total mass of the Venusian atmosphere compare to that of Earth?
- 2.2 How does the depth of the Venusian atmosphere compare to that of Earth? (Assume that the interiors of Venus and Earth have the same density)
- 2.3 Venus is smaller than the Earth and therefore exerts less gravitational pull on its atmosphere. Then how can the mass of its atmosphere be larger?

### 3. Gravitational separation of air

N<sub>2</sub> and O<sub>2</sub> have different molecular weights and therefore different scale heights in the atmosphere. This causes them to gravitationally separate. The separation takes place by molecular diffusion, while at the same time turbulent vertical mixing of air parcels tends to homogenize the N<sub>2</sub>/O<sub>2</sub> ratio, reversing the separation process.

Turbulent mixing can also be parameterized as a diffusion process. In surface air the molecular diffusion coefficient  $D \sim 10^{-1} \text{ cm}^2 \text{ s}^{-1}$  is considerably smaller than the turbulent diffusion coefficient  $K \sim 10^5 \text{ cm}^2 \text{ s}^{-1}$ . As a result, the N<sub>2</sub>/O<sub>2</sub> mixture does not significantly separate. However,  $D$  is inversely proportional to pressure while  $K$  varies relatively little with altitude. We assume here that  $K$  is constant with altitude.

- 3.1 Estimate the altitude at which gravitational separation becomes important in the atmosphere, as indicated by  $D$  and  $K$  being of same order of magnitude ( $D/K \sim 1$ )
- 3.2 Calculate the resulting maximum possible percentage increase in the N<sub>2</sub>/O<sub>2</sub> ratio per 10 km increase in altitude, assuming a temperature of 200 K.

## CHAPTER 3: SIMPLE MODELS

### 1. Short questions

- 1.1 Which of the following loss processes are first-order in atmospheric concentrations? (a) Photosynthetic uptake of CO<sub>2</sub> by the biosphere, (b) Photolysis of gases.
- 1.2 The Montreal Protocol has banned worldwide production of CFC-12. CFC-12 is removed from the atmosphere by photolysis with a lifetime of 100 years. Assuming compliance with the Protocol, and neglecting residual emissions from existing stocks, how long will it take for CFC-12 concentrations to drop to half of present-day values?
- 1.3 Consider a 2-box model for the atmosphere where one box is the troposphere (1000-150 hPa) and the other is the stratosphere (150-1 hPa). Assume a 2-year residence time for air in the stratosphere. What is the corresponding residence time of air in the troposphere?
- 1.4 Of the simple models presented in chapter 3, explain which one would be most appropriate for answering the following questions:
  - (a) Can the observed rise of atmospheric CO<sub>2</sub> concentrations be explained by the known rate of CO<sub>2</sub> emission from fossil fuel combustion?
  - (b) Large amounts of radioactive particles are released to the atmosphere in a nuclear power plant accident. What areas will be affected by this radioactive plume?
  - (c) An air pollution monitoring site suddenly detects high concentrations of a toxic gas. Where is this gas coming from?
  - (d) Will atmospheric releases of a new industrial gas harm the stratospheric ozone layer?

### 2. Observing the net US source of CO<sub>2</sub>

Consider a column model for transport across the contiguous US in which a column of air extending from the surface to 3 km altitude (taken as the top of the boundary layer) is transported from west to east across the US (total distance of 5,000 km from coast to coast) at a wind speed of 10 m s<sup>-1</sup>. The air density in this column is taken to be  $n_a = 2 \times 10^{19}$  molecules cm<sup>-3</sup>. The US fossil fuel source of CO<sub>2</sub> is 2.0 Pg C a<sup>-1</sup> and we assume it to be evenly distributed over the contiguous US surface area of 7x10<sup>6</sup> km<sup>2</sup>. Assuming no other source or sink of CO<sub>2</sub> in the US, calculate the resulting increase of CO<sub>2</sub> mixing ratio from the west coast to the east coast. With CO<sub>2</sub> monitoring instruments having 1 ppmv precision deployed on the both coasts, and assuming that the column model is correct, would you be able to determine whether or not land uptake of CO<sub>2</sub> in the US. is offsetting fossil fuel emission?

### 3. Aerosol scavenging by precipitation

Consider a box model for the US atmosphere with a constant source  $S$  of aerosol particles. The box is ventilated by a steady wind resulting in a residence time of 5 days for air in the box. Another pathway for removal of aerosol particles is by episodic precipitation. We assume that short rain events occur in the box every 5 days and that 100% of the aerosol is scavenged every time it rains.

- 3.1 Calculate the evolution of aerosol mass in the box over a 10-day period, starting from a mass of zero at time  $t = 0$ . Plot your result.
- 3.2 Calculate the time-averaged aerosol mass over that period.
- 3.3 We would like to simplify the treatment of aerosol lifetime in the box model by viewing the rain as a constant sink for aerosol with a rate constant  $k_r = 0.2 \text{ d}^{-1}$ . What would be the resulting steady state mass of aerosol in the box? How does it compare to the time-averaged aerosol mass calculated in question 2?

### 4. Ventilation of the eastern US

- 4.1 The dominant pathway for ventilation of pollution from the eastern US is by episodic cold fronts. Consider a 1-box model for the eastern US where ventilation occurs solely by these cold fronts. Every time a cold front passes the box is flushed instantaneously with clean air. Consider a pollutant in that eastern US box with a constant production rate  $P$  ( $\text{kg d}^{-1}$ ) and a first-order chemical loss rate constant  $k$  ( $\text{d}^{-1}$ ). Let  $T$  (d) be the period between passages of successive cold fronts. Plot qualitatively the temporal evolution of the mass  $m(t)$  of the pollutant in the box over the time interval  $[0, 2T]$  starting from an initial condition  $m(0) = 0$  immediately after a flushing event. Give an expression for the maximum mass  $m_{max}$  of the pollutant in the box.
- 4.2 Air quality agencies are concerned that climate change could affect the period  $T$  between cold front passages and hence the severity of air pollution events. For the model above, give an expression for  $dm_{max}/dT$  and show that the sensitivity of maximum pollutant accumulation (as measured by  $m_{max}$ ) to changes in  $T$  depends on the chemical lifetime of the pollutant. [Hint: briefly discuss the limiting cases  $k \rightarrow 0$  and  $k \rightarrow \infty$ ].

### 5. Using hydrocarbon pairs to infer OH concentrations

The hydroxyl radical (OH) is responsible for the oxidation of many atmospheric gases. Its concentration is very low and difficult to measure. We would like to estimate it indirectly. Consider a point source emitting hydrocarbons  $X_1, X_2, X_3$  to the atmosphere with emissions  $E_1, E_2, E_3$ . These hydrocarbons are removed from the atmosphere by oxidation by OH with rates  $-d[X_i]/dt = k_i[X_i][\text{OH}]$  where the rate constants  $k_i$  are in units of  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . We set up an observation site at a distance  $x$  downwind of the source and measure the concentrations of these three hydrocarbons. We interpret the observations with a puff model in which air parcels are transported from the point source to the observation site with a fixed wind

speed  $U$  while diluting with background air with a dilution rate constant  $k_d$  ( $\text{s}^{-1}$ ). Assume that the hydrocarbons have no other sources and that background concentrations are negligible.

- 5.1 Show that the mixing ratio  $C_I$  of hydrocarbon  $X_1$  measured at the observation site is given by

$$C_I = C_{I,o} \exp\left[\frac{-(k_1[\text{OH}] + k_d)x}{U}\right] \quad (1)$$

where  $C_{I,o}$  is the concentration at the source and  $[\text{OH}]$  is in units of molecules  $\text{cm}^{-3}$ .

- 5.2 Equation (1) could in principle be used to infer  $[\text{OH}]$ , but a practical problem is that  $C_{I,o}$  and  $k_d$  are not observable. We can get around this problem by using combined measurements for hydrocarbons  $X_1$  and  $X_2$ . Show that

$$[\text{OH}] = \frac{U}{(k_1 - k_2)x} \ln\left(\frac{E_1 C_2}{E_2 C_1}\right) \quad (2)$$

- 5.3 Equation (2) can be used to infer  $[\text{OH}]$  if the emission ratio  $E_2/E_1$  is known; however, this is often not the case. A way to get around this problem is to sample the plume over a range of wind speeds and plot  $\ln(C_2/C_1)$  vs.  $1/U$ . Show how this would work.
- 5.4 We wish to check that OH is indeed the main oxidant responsible for the loss of the hydrocarbons. For this purpose we need to bring in the third hydrocarbon  $X_3$ . Show that a plot of  $\ln(C_2/C_1)$  vs.  $\ln(C_3/C_1)$  has a slope  $(k_1 - k_2)/(k_1 - k_3)$ . How would you use that result to verify observationally that OH is indeed the main oxidant for the three hydrocarbons?

## 6. Fossil fuel combustion as a source of water vapor

Current global  $\text{CO}_2$  emission from fossil fuel combustion is  $7 \text{ Pg C a}^{-1}$ . The mean stoichiometric composition of the fuel burned is  $\text{CH}_{1.6}$  (one mole carbon per 1.6 moles hydrogen). We examine here if fossil fuel combustion is a significant source of atmospheric water vapor.

- 6.1 Write the stoichiometric reaction for the oxidation of  $\text{CH}_{1.6}$  by oxygen during combustion.
- 6.2 Knowing that the global precipitation rate is  $3 \text{ mm d}^{-1}$ , calculate the global source ( $\text{Pg a}^{-1}$ ) of water vapor to the atmosphere. Compare to the source of water vapor from fossil fuel combustion.
- 6.3 The fossil fuel source of water vapor could be relatively more significant in the stratosphere as a result of aviation. Assume that the air in the stratosphere accounts for 15% of total atmospheric mass, has a mean water vapor mixing ratio of 4 ppmv, and has a residence time of 1 year against transfer to the troposphere. Calculate the corresponding source ( $\text{Pg a}^{-1}$ ) of water vapor in the stratosphere. Considering that aircraft account for 2% of global fossil fuel combustion and that  $2/3$  of aircraft emissions are released in the stratosphere, calculate the fraction of the global

stratospheric water vapor source contributed by aircraft. Assume in your calculation that aviation fuel has a stoichiometry of  $\text{CH}_{1.6}$ , equal to the mean.

## CHAPTER 4: ATMOSPHERIC TRANSPORT

### 1. Short questions

- 1.1 In the movie *The Day After Tomorrow*, climatologist hero Jack Hall observes a mass of cold air from the upper troposphere descending rapidly to the surface and predicts that it will trigger an ice age over the United States. When another forecaster objects, “Won’t this air mass heat up as it sinks?”, our hero replies “It’s sinking too fast. It doesn’t have time”. Can our hero be right? Briefly explain.
- 1.2 A sea-breeze circulation often produces a temperature inversion. Explain why.
- 1.3 A well known air pollution problem is “fumigation” where areas downwind of a major pollution source with elevated stacks experience sudden bursts of very high pollutant concentrations in mid-morning. Can you explain this observation on the basis of atmospheric stability?
- 1.4 Consider an atmosphere that is unstable from the surface up to some altitude (top of mixed layer) and stable above. Show graphically that a plume from a surface fire will be injected into this atmosphere above the top of the mixed layer, and that the altitude of injection may depend on the water vapor content of the plume.
- 1.5 A persistent mystery in atmospheric chemistry is why the stratosphere is so dry (3-5 ppmv H<sub>2</sub>O). Based on water vapor concentrations observed just below the tropopause, one would expect the air entering the stratosphere to be moister. One theory is that very strong thunderstorms piercing through the tropopause can act as a “cold finger” for condensation of water and thereby remove water from the lower stratosphere. Explain how this would work.
- 1.6 Observed vertical profiles of trace gases emitted at the surface often show a “C-shape” over source regions, with high values in the lower and upper troposphere vs. low values in the middle troposphere. What transport mechanism is responsible for such a profile? Can it be simulated with a turbulent diffusion model?
- 1.7 A tower measures vertical fluxes of CO<sub>2</sub> 10 m above the top of a forest canopy. For a typical horizontal wind speed of 10 m s<sup>-1</sup> and turbulent diffusion coefficient  $K_z = 1 \times 10^4 \text{ cm}^2 \text{ s}^{-1}$ , estimate the distance upwind of the tower (the “fetch”) contributing to the CO<sub>2</sub> fluxes measured at the tower.

### 2. Cloud base altitude

We can estimate the cloud base altitude for a given atmosphere from the properties of surface air. Consider an air parcel at the Earth’s surface with temperature of 20°C and relative humidity of 30%. As this air parcel rises in the atmosphere it cools following the adiabatic lapse rate. We would like to determine the altitude at which it will form a cloud. Use the following equation for the saturation vapor pressure of water  $p_{H_2O,SAT}$  (hPa) as a function of temperature  $t_C$  (°C):

$$p_{H_2O,SAT} = 6.1 \exp\left[\frac{17.67t_c}{t_c + 243.5}\right]$$

- 2.1 If  $p_{H_2O}$  remained constant in the rising air parcel, calculate the altitude of cloud base.
- 2.2 In fact,  $p_{H_2O}$  decreases in the rising air parcel because of the decrease in atmospheric pressure. Assuming an atmospheric scale height  $H = 7.4$  km, determine the altitude of cloud base.

### 3. An atmosphere with fixed relative humidity?

- 3.1 Consider a hypothetical atmosphere with a vertically uniform mixing ratio of water vapor *and* a vertically uniform RH. Let  $p_{H_2O,SAT} = f(T)$  describe the dependence of saturation water vapor pressure on temperature. Using in addition the barometric law, derive an equation relating  $T$  to  $z$  in such an atmosphere.
- 3.2 Would such an atmosphere be stable or unstable? [Hint; never mind the equation you derived in question 1 – just think about what happens to RH in the real world when an air parcel rises]. Is the water vapor mixing ratio then likely to be uniform?

### 4. Scavenging in a convective updraft

We examine here how deep convection scavenges water-soluble species from the atmosphere. Consider a sea-level air parcel at 50% RH, 20°C lifted in a convective updraft without exchanging any material with its surroundings. Use the following equation for the saturation vapor pressure of water  $p_{H_2O,SAT}$  (hPa) over liquid as a function of temperature  $t_c$  (°C):

$$p_{H_2O,SAT} = 6.1 \exp\left[\frac{17.7t_c}{t_c + 243.5}\right]$$

- 4.1 Show that the air parcel will form a cloud at about 1 km altitude. [*Hint: you can ignore the relatively small change in atmospheric pressure between the surface and cloud base*]
- 4.2 This saturated air parcel keeps rising until it reaches the tropopause at 11 km altitude. Assuming a mean wet adiabatic lapse rate  $\Gamma_w = 6.5$  K km<sup>-1</sup>, show that the temperature in the cloud outflow at 11 km is -55°C.
- 4.3 The cloud outflow is saturated with respect to ice. The saturation water vapor pressure over ice at -55°C is 0.07 hPa. Show that 97% of the water in the initial air parcel has been scavenged by precipitation by the time the air parcel exits the cloud at 11 km altitude. [*Hint; you must account for the decrease in atmospheric pressure with altitude. Use a scale height  $H = 7.4$  km*].
- 4.4 Scavenging is even more efficient for water-soluble species such as aerosol particles. Consider an aerosol species 100% partitioned into cloudwater within a cloud. The convective updraft has an upward velocity of 5 m s<sup>-1</sup>, and cloudwater in the updraft is converted to precipitation with a rate constant  $k = 5 \times 10^{-3}$  s<sup>-1</sup>. Calculate the altitude above cloud base at which 99% of the aerosol species from the initial air parcel will have been scavenged. You should find  $z = 5.6$  km. Briefly explain why scavenging of such a water-soluble aerosol is even more efficient than scavenging of water itself.

## 5. Fumigation

Consider a box model for an urban airshed of arbitrary horizontal dimension and extending vertically from the surface to a mixing depth  $h$ . The mixing depth has a low value  $h_0$  at night, increases linearly with time from sunrise to noon at a rate  $dh/dt = a$ , remains constant at a value  $h_1$  from noon to sunset, and drops rapidly back to  $h_0$  at sunset. There is no transfer of air across the mixing depth.

- 5.1 Sketch the evolution of  $h$  as a function of time of day and give a brief physical explanation for this evolution.
- 5.2 We wish to determine how a pollutant originating from aloft would affect the urban airshed. Consider a pollutant present in the air above the mixing depth at a fixed concentration  $C'$ . The pollutant has no source within the urban airshed and is destroyed within the urban airshed with a first-order loss rate constant  $k$ . Show by simple reasoning that the concentration of the pollutant in the urban airshed must be maximum at some time in the morning hours (this is called “fumigation”).
- 5.3 Show that the concentration of the pollutant in the urban area during the morning hours is given by

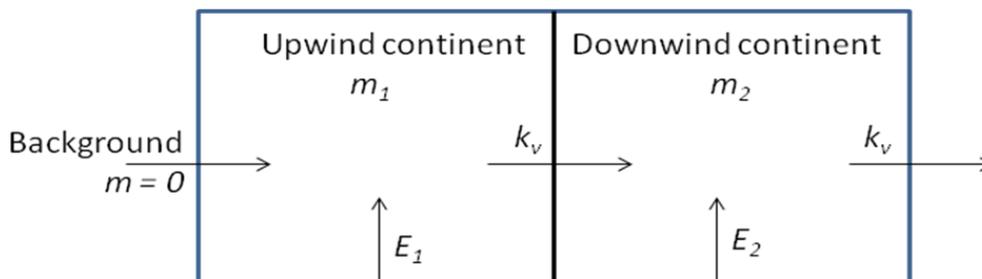
$$C = \frac{C_o h_o}{h_o + at} \exp[-kt] + \frac{aC'}{k(h_o + at)} (1 - \exp[-kt])$$

where  $C_o$  is the concentration at sunrise.

- 5.4 From the above equation, show that in the limit  $k \rightarrow \infty$  (short-lived pollutant) the concentration  $C$  is maximum at sunrise, while in the limit  $k \rightarrow 0$  (long-lived pollutant) the concentration is maximum at noon. [Hint: recall that  $e^{-x} \rightarrow 1-x$  as  $x \rightarrow 0$ ] Offer brief physical explanations for these two limits.

## 6. Intercontinental transport

Strategies to control air pollution through domestic emission controls may need to consider the effect of pollution transported from continents upwind. Consider a simple two-box model of an upwind continent (1) and a downwind continent (2) in a westerly flow as shown below.



In this model, the upwind and downwind continents are ventilated with the same first-order rate constant for ventilation  $k_v$ . The upwind continent is ventilated with clean background air while the downwind continent is ventilated with polluted air

from the upwind continent. Consider a pollutant with emissions  $E_1$  and  $E_2$  ( $\text{kg s}^{-1}$ ), and with a first-order loss rate constant for chemical loss  $k_C$  ( $\text{s}^{-1}$ ) that is the same for the upwind and downwind continents.

- 6.1 Express the steady-state pollutant masses  $m_1$  and  $m_2$  in the two continental boxes as functions of  $E_1$ ,  $E_2$ ,  $k_V$ , and  $k_C$ .
- 6.2 The Environmental Protection Agency (EPA) of continent 2 must decide if it should try to reduce its pollutant level  $m_2$  through domestic controls or through an international control agreement with continent 1. For this purpose, the EPA wishes to compare the relative benefit of domestic emission control ( $dm_2/dE_2$ ) to international emission control ( $dm_2/dE_1$ ). Derive an expression for the relative benefit of domestic vs. international emission control  $b = (dm_2/dE_2)/(dm_2/dE_1)$ . Compare the relative benefits for a very long-lived pollutant ( $k_C \rightarrow 0$ ) and a very short-lived pollutant ( $k_C \rightarrow \infty$ ).
- 6.3 Based on your knowledge of the time scales for westerly transport at northern mid-latitudes, conclude as to the relative benefit for the EPA to focus on domestic emission controls for its three pollutants of most concern: aerosols (lifetime 3 days), ozone (lifetime 2 weeks), and mercury (lifetime 6 months).

## CHAPTER 6: GLOBAL BIOGEOCHEMICAL CYCLES

### 1. Short questions

- 1.1 Denitrification seems at first glance to be a terrible waste for the biosphere, jettisoning precious fixed nitrogen back to the atmospheric  $\text{N}_2$  reservoir. In fact, denitrification is essential for maintaining life in the interior of continents. Can you see why?
- 1.2 Although volcanoes don't emit  $\text{O}_2$  they do emit a lot of oxygen (as  $\text{H}_2\text{O}$  and  $\text{CO}_2$ ). Both  $\text{H}_2\text{O}$  and  $\text{CO}_2$  photolyze in the upper atmosphere. Photolysis of  $\text{H}_2\text{O}$  results in production of atmospheric  $\text{O}_2$  but photolysis of  $\text{CO}_2$  does not. Why this difference?
- 1.3 Comparison of the rates of  $\text{CO}_2$  atmospheric accumulation vs. global fossil fuel emission indicates that only 50% of the  $\text{CO}_2$  emitted by fossil fuel combustion remains in the atmosphere. Does this mean that atmospheric  $\text{CO}_2$  has a lifetime of only about 1 year? Does this mean that  $\text{CO}_2$  would start declining if fossil fuel emissions were to stop tomorrow?
- 1.4 A famous politician suggested sarcastically that “we all quit breathing” to reduce the source of  $\text{CO}_2$  to the atmosphere. Would that work? Briefly explain.
- 1.5 Dead organisms sedimenting on the ocean floor have calcium carbonate ( $\text{CaCO}_3$ ) shells. Does the burial of the oxygen in these shells affect atmospheric oxygen?
- 1.6 Upwelling of deep ocean water supplies high concentrations of nutrients such as nitrogen to the surface ocean. What is the effect of this upwelling on atmospheric  $\text{CO}_2$ ?
- 1.7 As oceans acidify due to increasing  $\text{CO}_2$ , it will become more difficult for marine organisms to produce calcium carbonate shells. Briefly explain why.
- 1.8 The present-day fossil fuel source of  $\text{CO}_2$  to the atmosphere is  $8 \text{ Pg C a}^{-1}$ . 30% of that is removed by uptake by the ocean every year. Assume that this uptake is restricted to the surface ocean, 100-m deep and covering a global area of  $3 \times 10^{14} \text{ m}^2$ . The present-day  $\text{CO}_3^{2-}$  concentration in the surface ocean is  $2 \times 10^{-4} \text{ M}$ . What fraction of that  $\text{CO}_3^{2-}$  is consumed in a single year of fossil fuel input?
- 1.9 Melting of polar icecaps would reduce deep water formation and hence the transfer of  $\text{CO}_2$  to the deep ocean. Why?
- 1.10 It is proposed to reduce  $\text{CO}_2$  emissions by asking farmers to compost rather than burn their agricultural waste. Does this make sense?
- 1.11 From the standpoint of controlling atmospheric  $\text{CO}_2$ , is it better to heat your home with a wood stove or by natural gas?
- 1.12 The conventional scientific view is that fossil fuel  $\text{CO}_2$  injected to the atmosphere will affect the atmosphere for ~100 years before transfer to the deep ocean and that it represents therefore a long-term environmental problem. This view has been challenged by skeptics on the basis of bomb  $^{14}\text{CO}_2$  data. Above-ground nuclear tests in the 1950s injected large amounts of  $^{14}\text{CO}_2$  in the atmosphere, but atmospheric observations following the nuclear test ban in 1962 showed an

exponential decay of  $^{14}\text{CO}_2$  back to background values on a time scale of 5 years.

This shows, according to skeptics, that if we were to shut down fossil fuel emissions then  $\text{CO}_2$  would return to natural background values within 5 years.

What do you think of this reasoning?

- 1.13 You wish to fly from Boston to California on a commercial flight that consumes 100,000 lbs of jet fuel for the trip. The company offers - as an extra charge on your ticket - to make your personal trip carbon-neutral by planting trees. Does this seem practical, in terms of the number of trees that would need to be planted? And is this a reasonable long-term proposition for mitigating your personal “carbon footprint”?

## 2. Time scale for ocean mixing

Figure 6.9 from the book shows a four-box model of the global ocean circulation. The global mixing time of the ocean in that model is about 200 years. This is not immediately obvious, because...

- 2.1 Show that the residence time of water in the combined intermediate+deep ocean reservoir is 670 years, much longer than 200 years.
- 2.2 We are however interested in the mixing time, which is different than the residence time. Consider a simpler 2-box model for the ocean where water in reservoir 1 (mass  $m_1$ ) has a residence time  $\tau_1$  against transfer to reservoir 2, and water in reservoir 2 (mass  $m_2$ ) has a residence time  $\tau_2$  against transfer to reservoir 1. Show that the characteristic mixing time  $\tau$  for  $m_1$  and  $m_2$  to approach steady state is  $\tau = (\tau_1^{-1} + \tau_2^{-1})^{-1}$  [Hint: write a differential equation for  $dm_i/dt$  and make use of the fact that the total mass of tracer  $m_T = m_1 + m_2$  stays constant]. Is  $\tau$  larger or smaller than  $\tau_1$  and  $\tau_2$  ?
- 2.3 Use the result of 2.2.2 to calculate the mixing time of the ocean in two possible two-box model simplifications of Figure 6.9: (1: surface, 2: intermediate+deep) and (1: surface+intermediate, 2: deep).
- 2.4 You should obtain surprisingly short values (a few decades) in question 2.3. Explain qualitatively why the 2-box model would tend to underestimate the actual ocean mixing time.

*[Quantifying the actual mixing time for a 4-box model requires an eigenmode analysis. See chapter 3.2 of “Chemical Transport Models”, available on-line from my educational web site].*

## 3. Ocean alkalinity and $\text{CO}_2$ uptake

The alkalinity of the present-day ocean is  $2.3 \times 10^{-3}$  M. The pH is 8.2. Assume the ocean to be well mixed. Infer the  $\text{CO}_3^{2-}$  concentration in the ocean, using the equilibrium constant



Assuming that uptake of atmospheric CO<sub>2</sub> by the ocean conserves ocean alkalinity, show that this places an upper limit of 1600 ppmv for the total amount of additional atmospheric CO<sub>2</sub> that could be taken up by the ocean.

#### 4. How ducky is duct tape?

As a precaution against terrorist biological or chemical attacks, it has been suggested that U.S. households choose a room in the house as a shelter and seal it with plastic sheeting and duct tape. How long can we survive in such a closed environment? Consider a family of four in a large room 10x10 m<sup>2</sup> in area and 3 m in height. Each individual consumes 3 kg of oxygen per day. Assume an initial air pressure of 1000 hPa and a constant temperature of 298 K.

- 4.1 Our first concern is depletion of oxygen. Show that we will run out of oxygen in 7 days.
- 4.2 Before running out of oxygen, however, we might die from accumulation of CO<sub>2</sub>. At a mixing ratio of 0.03, CO<sub>2</sub> becomes toxic. Assuming no removal of CO<sub>2</sub> from the room, show that this level of CO<sub>2</sub> is reached in about a day.
- 4.3 We can attempt to remove this CO<sub>2</sub> chemically by continuously bubbling the air in the room through a water solution saturated with calcium carbonate (CaCO<sub>3</sub>). Explain briefly how this would work.
- 4.4 Would this bubbler also work to replenish O<sub>2</sub>? Briefly explain.

#### 5. Measuring CO<sub>2</sub> from space

Column concentrations of CO<sub>2</sub> can be measured from space by backscatter of near-IR solar radiation. This measurement must have very high precision if it is to be useful for quantifying carbon sources and sinks, since there is so little atmospheric variability of CO<sub>2</sub> concentrations. We examine here the specifications required for a satellite instrument to quantify surface carbon fluxes over East Asia. We consider a box model for the region extending 6000 km in the east-west direction, 3000 km in the north-south direction, and vertically from 1000 hPa up to the tropopause at 300 hPa. We assume the box to be well-mixed and to be ventilated by a westerly flow of 10 m s<sup>-1</sup>. We further assume that the air upwind contains a uniform background CO<sub>2</sub> mixing ratio.

- 5.1 The CO<sub>2</sub> surface flux in the East Asian region is estimated to peak in March at 1x10<sup>11</sup> mol day<sup>-1</sup> (net emission) and to be minimum in August at -1x10<sup>11</sup> mol day<sup>-1</sup> (net uptake). Show that the corresponding seasonal variation of the CO<sub>2</sub> mixing ratio in the region relative to the background is ± 0.2 ppm. Roughly what percentage of the CO<sub>2</sub> background does that represent? Measuring any gas with

better than 1% precision is difficult. We see that measuring CO<sub>2</sub> from space is a major challenge!

- 5.2 The satellite instrument doesn't actually measure a CO<sub>2</sub> mixing ratio but rather a column concentration  $\Omega_{\text{CO}_2}$  (molecules cm<sup>-2</sup>). Show that without simultaneous accurate knowledge of the local surface pressure the measurement would be useless.
- 5.3 A solution is to have the instrument measure the O<sub>2</sub> column concentration  $\Omega_{\text{O}_2}$  together with that of CO<sub>2</sub>, taking advantage of O<sub>2</sub> absorption features in the near-IR. Briefly explain how one can obtain CO<sub>2</sub> mixing ratio information in this manner.

## 6. Terrestrial sink of CO<sub>2</sub>

We examine here the constraints offered by atmospheric CO<sub>2</sub> observations on the rate of carbon uptake by the terrestrial biosphere.

- 6.1 Atmospheric CO<sub>2</sub> concentrations increased by 1.5 ppm a<sup>-1</sup> during the decade of the 1990s. During that time the fossil fuel source was 6.3 Pg C a<sup>-1</sup> and the net uptake by the ocean was 1.7 Pg C a<sup>-1</sup>. Show that this implies net uptake of carbon by the terrestrial biosphere of 1.4 Pg C a<sup>-1</sup>.
- 6.2 Mean observed CO<sub>2</sub> concentrations in the northern hemisphere are 2.5 ppm higher than in the southern hemisphere. Assume that the fossil fuel source of CO<sub>2</sub> is 95% in the northern hemisphere, and that the ocean sink is distributed among hemispheres following the areal ocean fraction (2/3 in the southern hemisphere and 1/3 in the northern hemisphere). Using a global 2-box model where one box is the northern hemisphere, the other is the southern hemisphere, and transport from one box to the other takes place with a rate constant  $k = 1 \text{ a}^{-1}$ , deduce that 80% of the net terrestrial biospheric sink must be located in the northern hemisphere. [Hint #1: treat uptake by the ocean and by the terrestrial biosphere as 0<sup>th</sup>-order loss processes since you know their global magnitudes. Hint #2: show that you can assume steady state for the difference in concentrations between the two hemispheres].
- 6.3 You should have found in question 2 that the calculated fraction of the terrestrial sink in the northern hemisphere is highly sensitive to the interhemispheric distribution of the fossil fuel source. Although the distribution of fossil fuel combustion is well known, 5% of that carbon is not directly emitted as CO<sub>2</sub> but instead as CO and methane, which are then oxidized to CO<sub>2</sub> with lifetimes of 2 months (CO) and 10 years (methane). Explain qualitatively how this would affect the interhemispheric distribution of the terrestrial carbon sink that you calculated in question 2.

# CHAPTER 7: CHEMICAL FORCING OF CLIMATE

## 1. Short questions

- 1.1 For an object of given volume, which shape emits the least radiation?
- 1.2 If the Earth were hollow, would it emit more or less radiation?
- 1.3 In our calculation of the effective temperature of the Earth we viewed the Earth as a blackbody. However, we also accounted for the fact that the Earth absorbs only 72% of solar radiation (albedo = 0.28), so obviously the Earth is not a very good blackbody (which would absorb 100% of all incoming radiation). Nevertheless, the assumption that the Earth emits as a blackbody is correct to within a few percent. How can you reconcile these two results?
- 1.4 The net radiative energy absorbed by the Earth surface averages  $99 \text{ W m}^{-2}$  over the globe. Part of this radiative energy is re-emitted to the atmosphere directly as heat, while the rest is used to evaporate water. The global precipitation rate on Earth is  $2 \text{ mm d}^{-1}$ , and the latent heat of vaporization of water is  $2.5 \times 10^6 \text{ J kg}^{-1}$ . Deduce the fraction of the net radiative energy at the Earth's surface that is used to evaporate water.
- 1.5 Soot particles absorb visible radiation but are transparent in the infrared. Explain how this can have either a warming or cooling effect on the Earth's surface depending on the altitude of the soot and the surface albedo.
- 1.6 Stratospheric ozone has both a cooling and warming effect on the Earth's surface temperature. Explain.
- 1.7 Fuel combustion emits water vapor. This water vapor has negligible greenhouse warming effect when emitted from cars in surface air, but it has a strong greenhouse warming effect when emitted from aircraft at the tropopause. Explain why.

## 2. Observing wildfires from space

The MODIS satellite instrument detects wildfires from space by measuring radiation emitted by the Earth at  $4.0 \text{ }\mu\text{m}$ . Let's understand how that works.

- 2.1 A typical wildfire has a temperature of 900 K. Show that the blackbody emission of radiation from the fire peaks at  $3.2 \text{ }\mu\text{m}$ .
- 2.2 It would seem logical then to detect wildfires by observing radiation at  $3.2 \text{ }\mu\text{m}$ , but in fact  $4.0 \text{ }\mu\text{m}$  is much better. Explain why. [*Hint: see Fig. 7-11 of book*]
- 2.3 At  $4.0 \text{ }\mu\text{m}$ , what is the ratio of blackbody emission of radiation from the wildfire at 900 K vs. a neighboring unburned area at 300 K? Conclude as to the ability of this technique to reliably detect wildfires.

### 3. Climate engineering with stratospheric sulfate aerosol

It has been proposed that global warming due to increasing CO<sub>2</sub> could be countered by injections of SO<sub>2</sub> in the stratosphere to produce sulfate aerosol.

- 3.1 It is estimated that injecting one ton of sulfur as SO<sub>2</sub> in the stratosphere would increase the albedo  $A$  of the Earth by  $\Delta A = 4 \times 10^{-8}$  for a duration of one year. Briefly explain what determines this one year time scale for the persistence of the effect.
- 3.2 Show that the corresponding radiative forcing  $\Delta F$  for that 1-year period would be  $1.4 \times 10^{-5} \text{ W m}^{-2}$ .
- 3.3 We would like to use these SO<sub>2</sub> injections to maintain the climate at its present state, canceling the effect of future growth of CO<sub>2</sub>. The present-day CO<sub>2</sub> concentration is 380 ppm with a growth rate of  $1.5 \text{ ppm a}^{-1}$ . The radiative forcing  $\Delta F$  ( $\text{W m}^{-2}$ ) from increasing the CO<sub>2</sub> mixing ratio from  $C_o$  to  $C$  can be approximated as  $\Delta F = 6.3 \ln (C/C_o)$ . Calculate the amount of sulfur that would need to be injected to the stratosphere in the first year of this program.
- 3.4 The business-as-usual scenario from IPCC projects a rise of CO<sub>2</sub> to 500 ppm by 2050. Calculate the amount of sulfur that will need to be injected to the stratosphere in 2050 to maintain climate at the condition we have today.

### 4. Remote sensing in the terrestrial infrared

A satellite measuring upwelling radiation emitted by the Earth in the terrestrial infrared (TIR) detects a combination of blackbody radiation emitted by the Earth's surface and radiation emitted by atmospheric gases. This measurement can provide information on gas concentrations but a challenge is to separate the radiation emitted by the gases from the radiation emitted by the Earth's surface. We examine this issue here. Consider for simplicity an atmosphere initially transparent in the TIR above a blackbody Earth surface of fixed temperature  $T_o$ . We add to that transparent atmosphere a certain mixing ratio  $C$  of a gas X in an elemental altitude band  $dz$  at temperature  $T_l$ . We assume that the gas is transparent to solar radiation but behaves as a blackbody in the TIR wavelength range. Let  $df$  represent the fraction of outgoing terrestrial radiation absorbed by the gas.

- 4.1 Show that the addition of the gas to the atmosphere decreases the TIR radiation flux sensed by the satellite by an amount  $dF = \sigma(T_o^4 - T_l^4)df$  where  $\sigma$  is the Stefan-Boltzmann constant.
- 4.2 Show that  $df = \gamma C n_a(0) \exp[-z/H] dz$  where  $\gamma$  is the absorption cross-section of the gas,  $n_a(0)$  is the surface air number density, and  $H$  is the scale height of the atmosphere. [We generally use  $\sigma$  as notation for the absorption cross-section but we use  $\gamma$  here to avoid confusion with the Stefan-Boltzmann constant]
- 4.3 Assume that the atmospheric temperature decreases with altitude at a fixed lapse rate  $\Gamma = -dT/dz$ . Show then that  $dF \approx \beta C z \exp[-z/H] dz$  where

$\beta = 4\gamma\sigma T_o^3 n_a(0)$  is independent of altitude. [Hint: make use of  $(1-x)^4 \approx 1-4x$  for  $x \ll 1$ ].

- 4.4 We define the sensitivity  $S$  of the satellite instrument to the gas as the change  $dF$  in outgoing terrestrial radiation per elemental mixing ratio column  $Cdz$  of the gas injected at altitude  $z$ , thus  $S = dF/(Cdz)$ . Using the result from the previous question, plot  $S$  vs.  $z$ . Show that the sensitivity of the satellite instrument is maximum when the gas is at  $z = H$ . Explain qualitatively why  $S \rightarrow 0$  as  $z \rightarrow 0$  and as  $z \rightarrow \infty$ .
- 4.5 Based on the answer to the previous question, would you consider remote sensing in the TIR to be a good approach for observation of surface air quality? For observation of intercontinental transport of pollution at high altitude?

## 5. Radiative forcing by aerosols

The radiative forcing from anthropogenic aerosols is very inhomogeneous because of the short lifetime of aerosols against deposition, and this can affect the climate response associated with aerosol sources. We compare here the regional and global radiative forcings from US anthropogenic aerosols. Consider a 1-box model for the contiguous US boundary layer exchanging air vertically with the background atmosphere. We refer to “US anthropogenic aerosols” as the aerosols originating from anthropogenic emissions in the US boundary layer. Aerosols in the US boundary layer have a lifetime of 3 days against scavenging by precipitation and a lifetime of 7 days against ventilation to the background atmosphere. Assume steady state for aerosols in the US boundary layer and in the background atmosphere.

- 5.1 What is the fraction of aerosols originating from the US boundary layer that is ventilated to the background atmosphere? You should find a value of 30%.
- 5.2 The lifetime of aerosols against scavenging by precipitation in the background atmosphere is 20 days, much longer than in the US boundary layer. Why this difference?
- 5.3 Calculate the fraction of the total atmospheric mass of US anthropogenic aerosols that is present in the US boundary layer (the rest is present in the background atmosphere; assume that the only aerosol sink in the background atmosphere is scavenging by precipitation). You should find a value of 26%.
- 5.4 The contiguous US account for 1.5% of the surface area of the Earth. If the global mean radiative forcing from US anthropogenic aerosols is  $-0.2 \text{ W m}^{-2}$ , calculate the mean regional radiative forcing from these aerosols over the contiguous US. Assume in this calculation that aerosol radiative forcing is proportional to the aerosol column mass concentration (mass per unit area), and that the radiative forcing over the contiguous US is solely contributed by the aerosol in the US boundary layer. You should find a value of  $-3.5 \text{ W m}^{-2}$ .
- 5.5 The negative radiative forcing from aerosols over the contiguous US is larger than the positive greenhouse forcing from long-lived greenhouse gases ( $+2.6 \text{ W m}^{-2}$ ). Does this mean that the contiguous US should be experiencing a net cooling as a result of anthropogenic influence? Briefly explain your answer.

## 6. Global warming potential of methane

A standard policy measure of the climatic impact of emissions of a greenhouse gas is the global warming potential (GWP). We define  $GWP_i(t_H)$  as the integrated radiative forcing over a time horizon  $[t_o, t_H]$  from the pulse emission of a unit mass  $\Delta m_i(t_o)$  of gas  $i$  at time  $t_o$ :

$$GWP_i(t_H) = \int_{t_o}^{t_H} \Delta F_i(t) dt$$

where  $\Delta F_i(t)$  is the radiative forcing at time  $t$  exerted by  $\Delta m_i(t)$ . The IPCC tabulates GWPs of many gases for  $t_H$  values of 20, 50, 100, and 500 years.

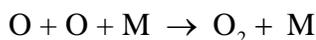
- 6.1 Give the units of GWP, and explain briefly how GWP calculated for  $t_H \rightarrow \infty$  provides a measure of the total heating resulting from the pulse emission of gas  $i$ .
- 6.2 Consider the GWP for methane. Methane is removed from the atmosphere by first-order loss with a corresponding atmospheric lifetime  $\tau = 10$  years. The radiative forcing from methane is found to be proportional to the square root of the mass perturbation:  $\Delta F_{CH_4}(t) = \alpha(\Delta m_{CH_4}(t))^{1/2}$  where  $\alpha$  is a constant. Plot  $GWP_{CH_4}(t_H)$  vs.  $t_H$ . At what time horizon  $t_H$  will 90% of the total heating from the methane emission pulse have been realized?
- 6.3 Consider a policy analyst faced with the task of controlling greenhouse gas emissions in order to reduce global warming over a time horizon  $t_H$ . Let  $E_i$  be the total emission of greenhouse gas  $i$  over  $[t_o, t_H]$ . Show that a suitable target for our policy analyst is to reduce  $\sum_i E_i GWP_i(t_H)$  where the sum is over all greenhouse gases.
- 6.4 This target can be achieved by different combinations of emission controls. Depending on the choice of time horizon, controlling methane emissions can be more attractive than controlling CO<sub>2</sub> emissions. Briefly explain.
- 6.5 It has thus been argued that controlling methane emissions could “buy us time” by allowing to delay CO<sub>2</sub> emission controls. However, there is a flaw in that reasoning. Let  $\Delta T(t)$  represent the global change in surface air temperature between  $t_o$  and  $t$ . Controlling methane emission would cause an immediate decrease in surface temperature. Explain how this near-term cooling would make methane emission control less effective in reducing the warming  $\Delta T(t_H)$  at the end of the time horizon. [Hint: think of how  $\Delta T$  affects the emission of terrestrial radiation to space]

## CHAPTER 10: STRATOSPHERIC CHEMISTRY

### 1. Short questions

- 1.1 Consider harmful UV radiation for which the ozone layer has an optical depth of 10. The ozone layer has thinned by 6% since 1970, with a corresponding 6% decrease in optical depth. What is the resulting percent increase in the flux of this UV radiation at the surface of the Earth?

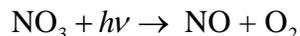
- 1.2 The original Chapman mechanism included a fifth reaction:



What is the effect of this reaction on ozone? Is it more important in the lower or in the upper stratosphere? Briefly explain. [*We don't include this reaction in the standard description of the Chapman mechanism because it is of negligible importance*]

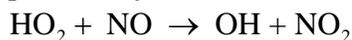
- 1.3 Would you expect O and O<sub>3</sub> concentrations in the stratosphere to vary with time of day, and if so how?

- 1.4 A minor branch of NO<sub>3</sub> photolysis is



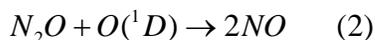
How does this reaction affect ozone?

- 1.5 Oxidation of NO to NO<sub>2</sub> can proceed by



What is the effect of this reaction of ozone? (Use the dominant loss pathways for each radical to complete the cycle)

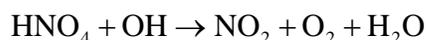
- 1.6 N<sub>2</sub>O in the stratosphere can react by two alternate pathways:



Show that competition between (1) and (2) lends stability to the ozone layer, i.e., acts as a negative feedback to an ozone perturbation.

- 1.7 It has been argued that a fleet of supersonic aircraft releasing NO<sub>x</sub> in the lower stratosphere would allow faster recovery of the stratospheric ozone layer over the coming decades. Briefly explain the argument.

- 1.8 Peroxynitric acid (HNO<sub>4</sub>) is produced and removed in the stratosphere by



What is the effect on stratospheric ozone? Think of the effects on both the NO<sub>x</sub> and HO<sub>x</sub> budgets.

- 1.9 Photochemical model calculations for the stratosphere including only the Chapman mechanism overestimate observed ozone levels by a factor of 3. However, in a budget calculation constrained by ozone observations we find that the  $O_3 + O$  reaction accounts for only 10% of the  $O_x$  sink. Can you reconcile these two results?
- 1.10 Satellite observations of ClO in the Antarctic stratosphere in the middle of winter show a “collar” of maximum values around 60°S. Why isn’t ClO highest over the South Pole, where temperatures would be lowest?

## 2. The discovery of the ozone layer

In a 1913 paper in the *Comptes Rendus de l’Academie des Sciences*, Fabry and Buisson reported the first measurements of the ozone absorption cross-section. They used a glass tube of pure ozone of length  $d$  at standard conditions of temperature and pressure (STP) ( $T = 273$  K,  $P = 1$  atm) and measured the attenuation of light as it passed through the tube. They reported their result in terms of an “absorption constant”  $\alpha$ ,

$$I = I_o 10^{-\alpha d}$$

and found that their data in the wavelength range 290-330 nm could be fitted by the function

$$\log \alpha = 17.58 - 0.0564\lambda$$

where  $\alpha$  is in units of  $\text{cm}^{-1}$  and  $\lambda$  is in units of nm.

- 2.1 Fabry and Buisson used their data to explain observations by Cornu (*Comptes Rendus*, 1881) that the minimum wavelength of detectable direct solar radiation at the ground varies as a function of solar zenith angle  $\theta$  as follows:

$$\lambda_{\min} = A - 20 \log(\cos \theta)$$

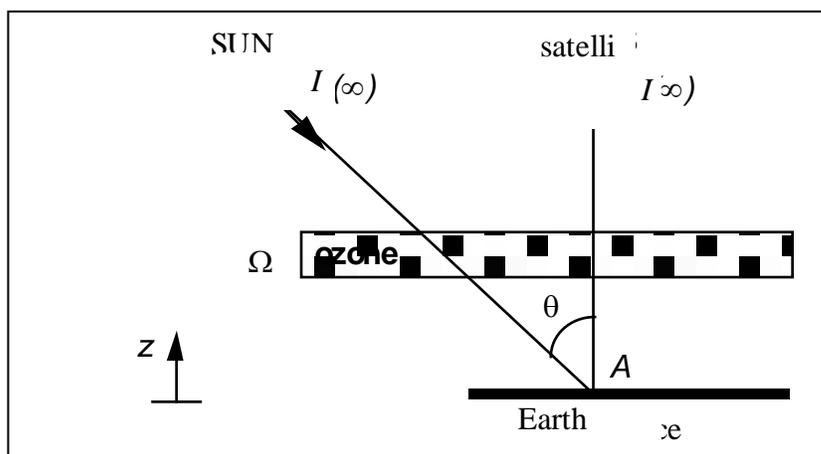
where  $A$  is a constant and  $\lambda_{\min}$  is in units of nm. Let  $I_o$  represent the solar radiation at the top of the atmosphere,  $I$  represent the direct solar radiation at the ground, and  $\lambda_{\min}$  represent the wavelength at which  $I/I_o = 1/n$  where  $n$  is some constant. Show that the observations of Cornu are consistent with absorption of solar radiation by ozone as determined from the absorption spectrum measured by Fabry and Buisson.

- 2.2 Fabry and Buisson went on to measure the attenuation of solar radiation at noon in Paris in summer ( $\theta = 30^\circ$ ) and observed  $I/I_o = 1/100$  at 300 nm. They inferred that the ozone column corresponded to a layer of pure ozone of 0.38 cm vertical thickness at STP. Show this.
- 2.3 They then calculated what surface mixing ratio this column would correspond to if ozone was well-mixed (uniform mixing ratio) in the atmospheric column. Calculate this mixing ratio, using an atmospheric scale height  $H = 7.4$  km and a surface air number density  $n_a(0) = 2.7 \times 10^{19}$  molecules  $\text{cm}^{-3}$ . How does it compare to typical ozone concentrations measured in background surface air?

[Epilogue: Fabry and Buisson concluded that “the most likely hypothesis is that ozone exists only in the upper atmosphere where it would be produced by extreme UV radiation that is absorbed by oxygen at lower altitudes”. Not bad for 1913!]

### 3. Measuring ozone from space

Ozone columns have been measured from space continuously since 1979 by backscatter of solar UV radiation. Consider a simple satellite instrument measuring reflected solar radiation at 340 nm and 380 nm wavelength. Ozone absorbs at 340 nm but not at 380 nm. Assume that there are no other atmospheric absorbers or scatterers at either of these wavelengths. Consider an atmosphere with a total  $O_3$  column  $\Omega$  (molecules  $cm^{-2}$ ) observed by the satellite directly overhead, with the downwelling solar radiation making an angle  $\theta$  to the vertical (solar zenith angle), as shown on the Figure.



Let  $I_S(\lambda)$  and  $I_R(\lambda)$  be the downwelling and reflected radiation at wavelength  $\lambda$ ,  $A$  the surface albedo (assumed identical at 340 and 380 nm), and  $\sigma$  the absorption cross-section of ozone (assumed constant). Show that the ozone column can be derived from the satellite measurements of reflected radiation by

$$\Omega = \frac{1}{\sigma \left( \frac{1}{\cos \theta} + 1 \right)} \ln \frac{I_R(\lambda_2) I_S(\lambda_1)}{I_S(\lambda_2) I_R(\lambda_1)}$$

where  $\lambda_1 = 340$  nm and  $\lambda_2 = 380$  nm.

### 4. Stratospheric water vapor increase

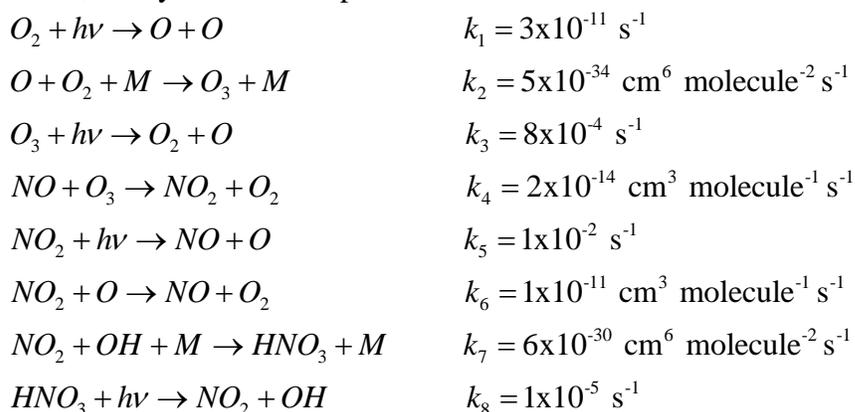
Stratospheric water vapor increased at a rate of  $1\% a^{-1}$  during the 1990s, for reasons that are unclear. Methane itself increased in the atmosphere at a rate of  $1\% a^{-1}$

during that period, and we examine here if this increase in methane could explain the increase in stratospheric water vapor. Consider a 2-box model for the troposphere + stratosphere system in which the residence times of air in the troposphere and the stratosphere are  $\tau_T = 10$  a and  $\tau_S = 2$  a, respectively. Methane is emitted from the surface at a rate  $E = 500 \text{ Tg a}^{-1}$ , and has a lifetime  $\tau = 10$  a against oxidation in both the troposphere and the stratosphere. Oxidation of one molecule of methane produces two molecules of water. Let  $m_T$  and  $m_S$  represent the masses of methane in the troposphere and the stratosphere, respectively. Write steady-state equations for  $m_T$  and  $m_S$ . Explain why the steady-state assumption is justified even though methane concentrations increase at a rate of  $1\% \text{ a}^{-1}$ . Solve to determine the source of stratospheric water vapor from the oxidation of methane in the stratosphere. You should find a value of about  $9 \text{ Tmol a}^{-1}$ .

*[The total amount of water vapor in the stratosphere is 100 Tmol, therefore the rise of methane has played only a minor role in the rise of water vapor. Increased transport of water vapor from the troposphere to the stratosphere must have been more important.]*

## 5. $\text{NO}_x$ -catalyzed ozone loss in the stratosphere

Consider an air parcel at 30 km altitude under mid-latitude equinox noontime conditions with  $T = 230 \text{ K}$ ,  $[\text{O}_3] = 2 \times 10^{12} \text{ molecules cm}^{-3}$ ,  $[\text{OH}] = 1 \times 10^7 \text{ molecules cm}^{-3}$ ,  $[\text{NO}] = 1 \times 10^9 \text{ molecules cm}^{-3}$ . Assume the following simplified mechanism to describe  $\text{NO}_x$ -catalyzed ozone depletion:



Rates for reactions (2) and (7) are at the low-pressure limit.

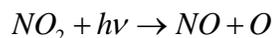
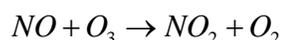
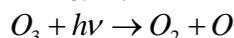
- 5.1 Calculate the steady-state concentrations of O and  $\text{NO}_2$  [Hint: make your life easier by considering only the most important reactions]. You should find  $[\text{O}] = 5 \times 10^7 \text{ molecules cm}^{-3}$ ,  $[\text{NO}_2] = 4 \times 10^9 \text{ molecules cm}^{-3}$ .
- 5.2 Calculate the rate of ozone loss by the  $\text{NO}_x$ -catalyzed cycle in this air parcel. Compare to the rate of  $\text{O}_3$  formation in the air parcel. What do you conclude?

- 5.3 Calculate the  $\text{NO}_x/\text{HNO}_3$  concentration ratio, assuming steady-state for  $\text{HNO}_3$ . Comment on the importance of  $\text{HNO}_3$  as a  $\text{NO}_x$  reservoir. If  $\text{HNO}_3$  formation did not take place, how much faster would  $\text{NO}_x$ -catalyzed ozone loss be?

## 6. Expanding the definition of the odd oxygen family

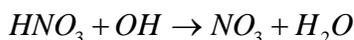
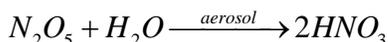
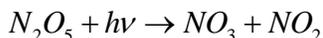
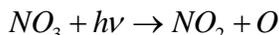
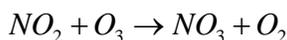
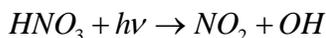
Accounting for the sources and sinks of ozone in the stratosphere can be made easier by expanding the odd oxygen ( $\text{O}_x$ ) family from its original  $\text{O}_x \equiv \text{O}_3 + \text{O}$  definition. The directing idea is that since  $\text{O}_x$  is produced from  $\text{O}_2$ , then the loss of  $\text{O}_x$  should involve reconversion to  $\text{O}_2$ . We consider here the application of this idea to nitrogen oxides.

- 6.1 Consider first the cycling between  $\text{O}_3$ ,  $\text{O}$ , and  $\text{NO}_2$  by the dominant null cycles:



Explain why it would make sense to include  $\text{NO}_2$  as part of the  $\text{O}_x$  family so that  $[\text{O}_x] = [\text{O}_3] + [\text{O}] + [\text{NO}_2]$ .

- 6.2 We showed in class that the rate of  $\text{NO}_x$ -catalyzed ozone loss is given by twice the rate of the  $\text{NO}_2 + \text{O}$  reaction. Show that this result can be immediately derived by considering  $\text{NO}_2$  as part of the  $\text{O}_x$  family.
- 6.3 One can further expand the  $\text{O}_x$  family by including  $\text{NO}_3$ ,  $\text{N}_2\text{O}_5$ , and  $\text{HNO}_3$  as members. Consider the following mechanism cycling  $\text{NO}_y$  species in the stratosphere:



By considering the null cycles in this mechanism, show that the definition of the  $\text{O}_x$  family can be expanded usefully as follows:

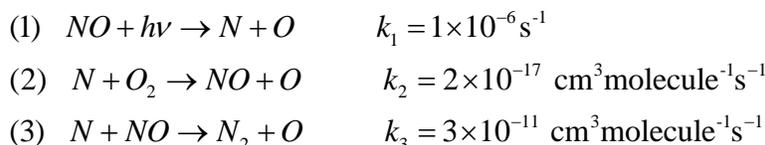
$$[\text{O}_x] = [\text{O}_3] + [\text{O}] + [\text{NO}_2] + [\text{HNO}_3] + 2[\text{NO}_3] + 3[\text{N}_2\text{O}_5]$$

Explain the multiplicative coefficients for  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$ .

- 6.4 Using this expanded definition of the  $\text{O}_x$  family, identify a cycle involving  $\text{HNO}_3$  formation and loss that represents a source of  $\text{O}_3$  and one that represents a sink of  $\text{O}_3$ .

## 7. Chemical loss of NO<sub>y</sub> in the upper stratosphere

The reactive nitrogen oxides family (NO<sub>y</sub>) responsible for catalytic loss of stratospheric ozone is removed from the stratosphere by transport to the troposphere (once in the troposphere, NO<sub>y</sub> is efficiently scavenged by precipitation). An additional sink for stratospheric NO<sub>y</sub> is chemical loss in the upper stratosphere, where strong UV radiation enables photolysis of NO:



We examine here the importance of this chemical sink for the stratospheric NO<sub>y</sub> budget.

- 7.1 For a typical NO<sub>y</sub> concentration of 15 ppb at 40 km altitude, show that Rate (2) >> Rate (3).
- 7.2 Assuming that N atoms are in steady state and that Rate (2) >> Rate (3), show that the NO<sub>y</sub> chemical loss rate  $L(\text{NO}_y)$  (molecules cm<sup>-3</sup> s<sup>-1</sup>) is given by

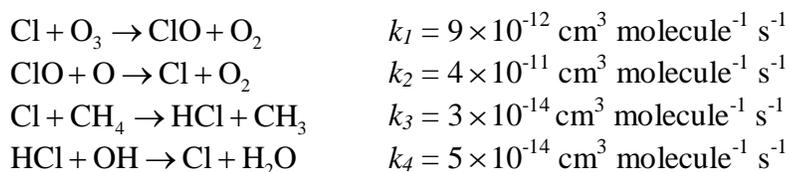
$$L(\text{NO}_y) = \frac{2k_1k_3f^2}{k_2[\text{O}_2]}[\text{NO}_y]^2$$

where  $f$  is the fraction of NO<sub>y</sub> present as NO.

- 7.3 Calculate the resulting lifetime of NO<sub>y</sub> against chemical loss at 40 km altitude, assuming the following typical conditions:  $k_1 = 1 \times 10^{-6} \text{ s}^{-1}$ ,  $k_2 = 2 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,  $k_3 = 3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,  $[\text{NO}_y] = 15 \text{ ppb}$ ,  $f = 0.5$ . You should find a NO<sub>y</sub> lifetime of 0.6 years.
- 7.4 Assuming that this chemical sink operates only in the upper stratosphere above 10 hPa, and that NO<sub>y</sub> is well mixed in the stratosphere, comment qualitatively on its importance relative to the loss of stratospheric NO<sub>y</sub> by transfer to the troposphere.

## 8. Ozone depletion potential of halocarbons

Consider the following simplified mechanism for chlorine chemistry in the stratosphere:



with typical concentrations (30 km altitude, 30°N, spring)  $[\text{O}_3] = 3 \times 10^{12} \text{ molecules cm}^{-3}$ ,  $[\text{O}] = 2 \times 10^7 \text{ molecules cm}^{-3}$ ,  $[\text{CH}_4] = 7 \times 10^{11} \text{ molecules cm}^{-3}$ ,  $[\text{OH}] = 2 \times 10^6 \text{ molecules cm}^{-3}$ .

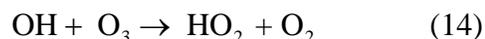
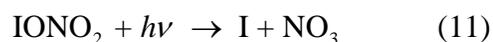
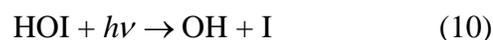
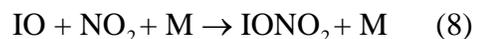
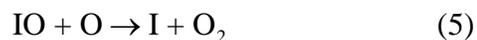
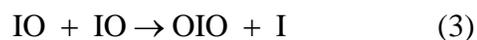
- 8.1 Assuming steady state for all  $\text{Cl}_y$  species, calculate the fractional contribution of each species to total  $\text{Cl}_y$ .
- 8.2 We define the *ozone depletion efficiency* of chlorine as the total number of ozone molecules destroyed by a molecule of  $\text{Cl}_y$  in the stratosphere before this  $\text{Cl}_y$  is ultimately transported to the troposphere and removed by deposition. Calculate the ozone depletion efficiency of chlorine by making the following assumptions:
- The conditions given at the beginning of the problem apply to the whole stratosphere;
  - The lifetime of air in the stratosphere is 2 years;
  - Chlorine transported to the troposphere is removed by deposition.
- 8.3 Other halogen atoms ( $X \equiv \text{F}, \text{Br}, \text{I}$ ) destroy ozone by catalytic mechanisms similar to Cl but with greatly different efficiencies dependent on the stability of the HX species. The electronegativity decreases from F to I so that the stability of HX decreases from F to I. Reaction of HF with OH is negligibly slow, while reactions of HBr and HI with OH have rate constants of  $1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively. There are no other significant sinks for HX. Assume that all reaction rate constants are the same for the different halogens except for the reaction  $\text{HX} + \text{OH}$ . Make rough quantitative estimates (no detailed calculations) of the ozone depletion efficiencies of the different halogens.
- 8.4 A standard industry index for the effect of a given chemical compound on the stratospheric ozone layer is the “ozone depletion potential” (ODP), defined as the depletion  $\Delta[\text{O}_3]$  of stratospheric  $\text{O}_3$  resulting from the emission of 1 kg of that compound, *relative* to the depletion  $\Delta[\text{O}_3]_{\text{CFC11}}$  resulting from emission of 1 kg of  $\text{CFC1}_3$  (CFC-11):

$$\text{ODP} = \frac{\Delta[\text{O}_3]}{\Delta[\text{O}_3]_{\text{CFC11}}}$$

Consider  $\text{CHClF}_2$  (HCFC-22), a CFC replacement compound of growing industrial use. HCFC-22 is removed from the atmosphere by oxidation by OH with a lifetime of 12 years in the troposphere and 44 years in the stratosphere. Oxidation of HCFC-22 releases the Cl atom. Assume that HCFC-22 is well-mixed throughout the atmosphere and that the stratosphere contains 15% of total atmospheric mass. Estimate the ODP of HCFC-22, using the same assumptions as in question 2. [Atomic weights:  $\text{H} = 1 \text{ g mol}^{-1}$ ,  $\text{C} = 12 \text{ g mol}^{-1}$ ,  $\text{Cl} = 35.5 \text{ g mol}^{-1}$ ,  $\text{F} = 19 \text{ g mol}^{-1}$ ].

## 9. Iodine chemistry

Iodine radicals are produced in the stratosphere by photolysis of methyl iodide ( $\text{CH}_3\text{I}$ ) emitted by the oceans. Consider the following mechanism for iodine chemistry:



- 9.1 Draw a diagram of the iodine cycle by the above mechanism. Identify which iodine species are radicals.
- 9.2 Identify three catalytic cycles for ozone loss.
- 9.3 Determine the rate-limiting step for each of the catalytic cycles for ozone loss, and write an overall equation for the ozone loss rate  $-d[\text{O}_3]/dt$  by the three cycles.

# CHAPTER 11: GLOBAL TROPOSPHERIC CHEMISTRY

## 1. Short questions

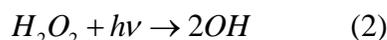
- 1.1 How does a thinning of the stratospheric ozone layer affect tropospheric OH concentrations?
- 1.2 HO<sub>x</sub> catalyze ozone destruction in the stratosphere but ozone production in the troposphere. Why the difference?
- 1.3 The rate constant for oxidation of alkanes C<sub>n</sub>H<sub>2n+2</sub> by OH increases rapidly with increasing *n*. Why is this?
- 1.4 If the CO source to the atmosphere were to double, would the CO concentration (a) double, (b) less than double, (c) more than double?
- 1.5 If the NO<sub>x</sub> source to the atmosphere were to double, would the NO<sub>x</sub> concentration (1) double, (2) less than double, or (3) more than double?
- 1.6 Methane has an atmospheric lifetime of about 10 years. However, estimates of the global warming potential from methane emissions assume a lifetime of 17 years for decay of this added methane. Why is that?
- 1.7 Maximum photon flux during summer results in a seasonal maximum of ozone in polluted regions but a seasonal minimum of ozone in very clean regions. Briefly explain.
- 1.8 When NO<sub>x</sub> concentrations are sufficiently high, PAN formation does not depend on NO<sub>x</sub> but instead increases with increasing ozone. Explain.

## 2. HO<sub>x</sub> radical loss catalyzed by Cu/Fe cycling in aqueous aerosols

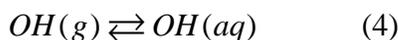
The dominant gas-phase sink for HO<sub>x</sub> radicals in the troposphere is



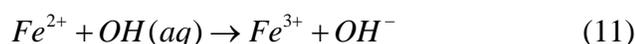
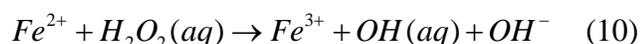
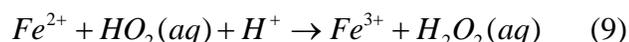
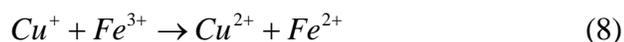
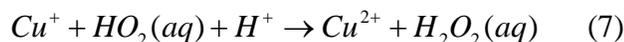
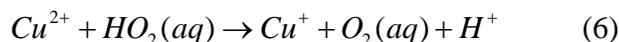
However, this is not a terminal sink because H<sub>2</sub>O<sub>2</sub> can be photolyzed back to HO<sub>x</sub> radicals:



Atmospheric observations suggest that loss of HO<sub>x</sub> radicals is faster than would be expected from reaction (1). It has been proposed that a more efficient loss could be driven by dissolution of HO<sub>2</sub> in aqueous aerosols and subsequent reactions involving redox cycling of copper and iron ions. Consider the three Henry's law equilibria by which HO<sub>2</sub>, OH, and H<sub>2</sub>O<sub>2</sub> can enter the aqueous aerosol phase, and assume that any aqueous-phase production of these species is followed by volatilization:



Redox cycling of Cu and Fe in aqueous aerosols is described by the following mechanism:



- 2.1 Write four different catalytic Cu and Fe catalytic cycles starting from reaction (6) and briefly explain how each of these would contribute to HO<sub>x</sub> loss.
- 2.2 Does the presence of Fe in the aerosol increase HO<sub>x</sub> loss relative to the presence of Cu alone?

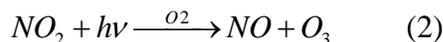
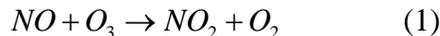
### 3. Radiative forcing of NO<sub>x</sub> and methane

- 3.1 Explain three ways in which NO<sub>x</sub> emissions can affect climate, and the sign of the associated radiative forcing for each.
- 3.2 The radiative forcing from anthropogenic methane in the present-day vs. pre-industrial atmosphere is 0.5 W m<sup>-2</sup> when referenced to the increase in methane *concentration* but 0.85 W m<sup>-2</sup> when referenced to methane anthropogenic *emission*. Explain the difference.
- 3.3 Tropospheric ozone is of concern both as a surface air pollutant and as a greenhouse gas. On a global scale, the ozone concentration is mainly determined by the abundance of NO<sub>x</sub> and methane. Explain briefly why methane is important in determining the global ozone concentration even though the ozone production rate is NO<sub>x</sub>-limited.
- 3.4 A strategy to reduce global tropospheric ozone from both a pollution and climate perspective must focus on reducing methane emissions rather than NO<sub>x</sub>. However, a strategy to reduce ozone smog locally must focus on reducing NO<sub>x</sub> emissions rather than methane. Explain these two apparently contradictory statements.

### 4. Ozone production from lightning

Lightning NO<sub>x</sub> is a very efficient source of tropospheric ozone because it is emitted in the upper troposphere where the lifetime of NO<sub>x</sub> is long. Assume that the loss of NO<sub>x</sub> is by conversion of NO<sub>2</sub> to HNO<sub>3</sub>.

- 4.1 Show that the lifetime of  $\text{NO}_x$  is proportional to  $(1 + \frac{[\text{NO}]}{[\text{NO}_2]})$
- 4.2 The  $\text{NO}/\text{NO}_2$  concentration ratio is largely controlled by the null cycle



Derive from this mechanism an expression for the  $\text{NO}/\text{NO}_2$  concentration ratio as a function of  $k_1$ ,  $k_2$ , and  $[\text{O}_3]$ . Calculate the value of this ratio in the upper troposphere (10 km altitude,  $T = 220$  K, 80 ppb  $\text{O}_3$ ) and in surface air (0 km,  $T = 300$  K, 30 ppb  $\text{O}_3$ ) using  $k_1 = 2 \times 10^{-12} \exp[-1400/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,  $k_2 = 1 \times 10^{-2} \text{ s}^{-1}$ , and a scale height  $H = 7.4$  km. You should find that the  $\text{NO}/\text{NO}_2$  concentration ratio is much larger in the upper troposphere than in surface air, implying a much longer lifetime for  $\text{NO}_x$ .

## 5. Mapping $\text{NO}_x$ emissions using satellites

Nitrogen dioxide ( $\text{NO}_2$ ) has strong absorption lines at 400-450 nm that allow satellite measurement of its atmospheric column by solar backscatter. We are interested in using this measurement to determine surface emissions of  $\text{NO}_x$ .

- 5.1 We first examine the relative contributions of the troposphere and the stratosphere to the total mass of  $\text{NO}_x$  in the atmosphere. The global emission of  $\text{NO}_x$  to the troposphere,  $E_{\text{NO}_x}$ , is about  $50 \text{ Tg N a}^{-1}$ . Assuming a lifetime  $\tau_{\text{NO}_x} = 1$  day against oxidation to  $\text{HNO}_3$ , and further assuming that  $\text{HNO}_3$  is removed solely by deposition, calculate the mass of  $\text{NO}_x$  in the troposphere.
- 5.2 The global mean mixing ratio of  $\text{N}_2\text{O}$  is 310 ppb and the atmospheric lifetime of  $\text{N}_2\text{O}$  is 114 years. All of the  $\text{N}_2\text{O}$  loss is in the stratosphere. Assuming that 5% of  $\text{N}_2\text{O}$  loss produces  $\text{NO}_x$ , that the  $\text{NO}_x/\text{NO}_y$  molar ratio in the stratosphere is 0.1, and that the lifetime of  $\text{NO}_y$  in the stratosphere is 1 year, estimate the mass of  $\text{NO}_x$  in the stratosphere. You should find that this mass is less than that in the troposphere but is not negligible.
- 5.3 We can remove the contribution of the stratosphere in various ways. After this subtraction we are left with a measurement of the tropospheric column  $\Omega$  of  $\text{NO}_2$ . Express  $\Omega$  as a function of local values of  $E_{\text{NO}_x}$ ,  $\tau_{\text{NO}_x}$ , and  $[\text{NO}_2]/[\text{NO}_x]$ , assuming local steady state for  $\text{NO}_x$  and further assuming that  $\tau_{\text{NO}_x}$  and  $[\text{NO}_2]/[\text{NO}_x]$  are uniform in the column.
- 5.4 A complication is that the  $[\text{NO}_2]/[\text{NO}_x]$  ratio varies with altitude, mostly because of the temperature dependence of the  $\text{NO} + \text{O}_3$  reaction. We can estimate this ratio on the basis of the rapid chemical cycling between  $\text{NO}$  and  $\text{NO}_2$ :



with rate constants  $k_1 = 2 \times 10^{-12} \exp[-1400/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $k_2 = 1 \times 10^{-2} \text{ s}^{-1}$ . Assuming a uniform  $\text{O}_3$  mixing ratio of 50 ppb, calculate the  $[\text{NO}_2]/[\text{NO}_x]$  ratio at sea level ( $T = 290 \text{ K}$ ) and at 10 km altitude ( $T = 220 \text{ K}$ ). On the basis of this result, would you expect the satellite to more easily detect emissions of  $\text{NO}_x$  at the surface, or in the upper troposphere (such as from lightning?)

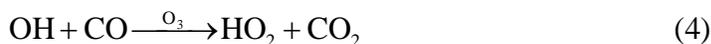
## 6. Chemical regimes in the upper troposphere

Aircraft emissions of  $\text{NO}_x$  may increase ozone concentrations in the upper troposphere where it is an efficient greenhouse gas. We examine here the sensitivity of ozone to  $\text{NO}_x$  in the upper troposphere under different conditions. The  $\text{NO}_x$  radicals ( $\text{NO}_x \equiv \text{NO} + \text{NO}_2$ ) cycle through the reactions:



Assume that the  $[\text{NO}]/[\text{NO}_2]$  ratio is determined solely by reactions (1)-(2) (a reasonable approximation in the upper troposphere). For the rest of this problem, write  $[\text{NO}] = \alpha[\text{NO}_x]$  and  $[\text{NO}_2] = (1-\alpha)[\text{NO}_x]$  where  $\alpha$  is a coefficient assumed constant.

The  $\text{HO}_x$  radicals ( $\text{HO}_x \equiv \text{OH} + \text{HO}_2$ ) in the upper troposphere are produced at a rate  $P(\text{HO}_x)$  that we assume to be constant. They cycle and are consumed principally by the following reactions:

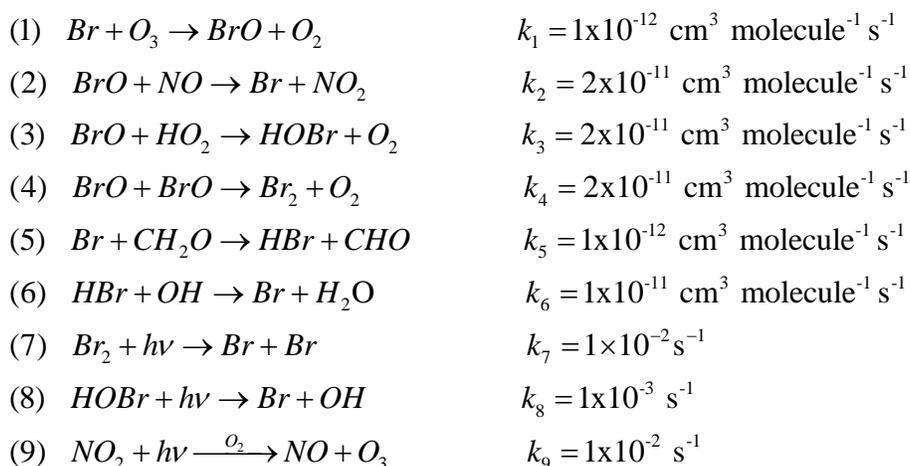


- 6.1 Identify four different  $\text{HO}_x$  sinks in the above mechanism.
- 6.2 We can distinguish four different chemical regimes in the upper troposphere depending on the dominant reaction for  $\text{HO}_x$  loss. Let us model each of these regimes by considering the limiting case where loss of  $\text{HO}_x$  is exclusively by the dominant reaction. Further assume that the  $\text{HO}_x$  radicals are in chemical steady state, and that  $\text{HO}_x$  cycling is efficient so that the  $\text{HO}_x$  cycling reactions are much faster than the  $\text{HO}_x$  loss reactions. For each regime, determine the dependence of the ozone production rate on  $[\text{NO}_x]$ .
- 6.3 Which of the four regimes applies to very low  $\text{NO}_x$  concentrations? to very high  $\text{NO}_x$  concentrations? Plot qualitatively the  $\text{O}_3$  production rate as a function of

[NO<sub>x</sub>], identifying each chemical regime in the plot. Briefly conclude as to the challenge of predicting the response of O<sub>3</sub> to increasing aircraft NO<sub>x</sub> emissions.

## 7. Tropospheric bromine

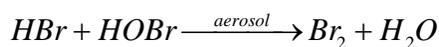
Satellite observations indicate a mean BrO concentration of 1 ppt in the troposphere. BrO at this level could represent an important tropospheric ozone sink. The dominant source of BrO in the troposphere is thought to be the photolysis and oxidation of bromoform (CHBr<sub>3</sub>) emitted naturally by the ocean biosphere. We examine here whether this source can account for the observed BrO. Consider the following mechanism for chemical cycling of the inorganic bromine family Br<sub>y</sub> (Br<sub>y</sub> ≡ Br + BrO + HBr + HOBr + 2Br<sub>2</sub>):



Assume the following concentrations: [O<sub>3</sub>] = 1 × 10<sup>12</sup> molecules cm<sup>-3</sup>, [NO] = 1 × 10<sup>9</sup> molecules cm<sup>-3</sup>, [HO<sub>2</sub>] = 1 × 10<sup>8</sup> molecules cm<sup>-3</sup>, [OH] = 1 × 10<sup>6</sup> molecules cm<sup>-3</sup>, [CH<sub>2</sub>O] = 2 × 10<sup>9</sup> molecules cm<sup>-3</sup>, and air density  $n_a = 1 \times 10^{19}$  molecules cm<sup>-3</sup>. It can be shown that cycling between Br and BrO by reactions (1) and (2) is much faster than any of the other reactions in the bromine mechanism and you may use that result in what follows.

- 7.1 The mean concentration of CHBr<sub>3</sub> observed in the troposphere is 0.7 ppt. CHBr<sub>3</sub> has an atmospheric lifetime of 10 days against chemical loss, releasing three Br atoms that go on to cycle with other Br<sub>y</sub> species by the above mechanism. Br<sub>y</sub> is eventually removed from the atmosphere by wet deposition with a lifetime of 10 days. Show that the resulting steady-state mean concentration of Br<sub>y</sub> is 2.1 ppt.
- 7.2 Draw a diagram of the Br<sub>y</sub> chemical mechanism described above. Identify radical and non-radical Br<sub>y</sub> species. Show that cycling between Br and BrO by reactions (1) and (2) is much faster than the competing reactions for Br and BrO. Identify two catalytic cycles for ozone destruction in the mechanism and identify the rate-limiting step for each.
- 7.3 Let BrO<sub>x</sub> ≡ Br + BrO represent the bromine radical family. From steady state between reactions (1) and (2) show that [Br]/[BrO] = 0.02.

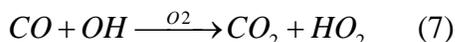
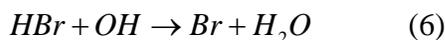
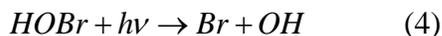
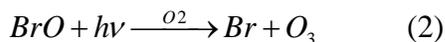
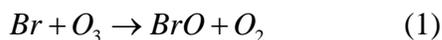
- 7.4 Calculate the resulting BrO concentration assuming that all Br<sub>y</sub> species are in steady state. [HINT: use steady-state equations to calculate the [HBr]/[BrO<sub>x</sub>] and [HOBr]/[BrO<sub>x</sub>] ratios, making use of [BrO] ≈ [BrO<sub>x</sub>] and [Br] ≈ 0.02 [BrO<sub>x</sub>]. For Br<sub>2</sub>, simply show that [Br<sub>2</sub>] ≪ [BrO<sub>x</sub>] so that Br<sub>2</sub> is a negligible component of Br<sub>y</sub>. You should find [BrO] = 0.3 ppt.
- 7.5 It has been proposed that the following reaction of HOBr with HBr in aerosols would increase BrO concentrations relative to the above mechanism:



Explain why this reaction would increase the BrO concentration.

## 8. Bromine chemistry in the present and pre-industrial troposphere

Consider the following mechanism for bromine chemistry in the troposphere:



- 8.1 Draw a diagram of the cycling between bromine species by this mechanism; identify which species are radicals.
- 8.2 Identify in this mechanism a catalytic cycle for ozone loss and the corresponding rate-limiting step for ozone loss. [Hint: assume that rate(7) ≫ rate(6)]
- 8.3 The preindustrial atmosphere contained less methane than today; would this cause the bromine-catalyzed ozone loss rate to be faster or slower than today? Briefly explain. [Hint: think of how methane affects CH<sub>2</sub>O]

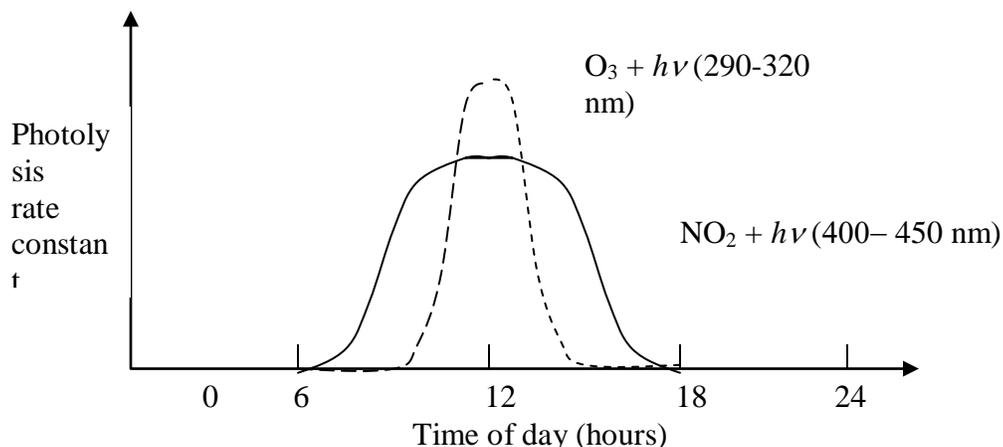
## CHAPTER 12: OZONE POLLUTION

### 1. Short questions

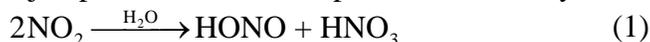
- 1.1 Atmospheric measurements of the  $\text{H}_2\text{O}_2/\text{HNO}_3$  concentration ratio offer a simple diagnostic of whether ozone production in a polluted environment is  $\text{NO}_x$ -limited or VOC-limited. Explain briefly why.
- 1.2 Atmospheric emission of ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) is increasing because of its use as a replacement fuel for gasoline. Write a possible reaction mechanism for oxidation of ethanol all the way to  $\text{CO}_2$ . Assume that peroxy radicals react only with  $\text{NO}$ . Deduce from your mechanism the number of ozone molecules produced from complete oxidation of one ethanol molecule.
- 1.3 Imagine an atmosphere where the dominant  $\text{HO}_x$  radical sink is the  $\text{RO}_2 + \text{NO}_2$  reaction to form stable peroxy nitrates. Would ozone production in such an atmosphere be  $\text{NO}_x$ -limited or VOC-limited?
- 1.4 A linear regression of the  $[\text{O}_3]$  vs.  $[\text{NO}_y]-[\text{NO}_x]$  relationship at a polluted site in a  $\text{NO}_x$  source region provides an estimate of the ozone production efficiency. Explain why.
- 1.5 PAN formation decreases the ozone production efficiency in a  $\text{NO}_x$  source region but increases the ozone production efficiency on a global scale. Explain why.

### 2. Radical generation in urban smog

The build-up of ozone in urban areas over the course of the day is strongly dependent on the availability of  $\text{HO}_x$  radicals during the morning hours. The source of  $\text{HO}_x$  radicals from ozone photolysis is not efficient until fairly late in the morning, as shown in the diagram below which compares the rate constants for  $\text{NO}_2$  photolysis and  $\text{O}_3 \rightarrow \text{O}(^1\text{D})$  photolysis as a function of time of day:



- 2.1 Explain why O<sub>3</sub> photolysis does not increase as rapidly as NO<sub>2</sub> photolysis following sunrise. [Hint: the optical depth of the atmosphere is much larger at 290-320 nm than at 400-450 nm]
- 2.2 It has been proposed that NO<sub>2</sub> reaction in aqueous aerosols, producing nitrous acid (HONO) could jump-start urban ozone production in early morning:



Assuming that photolysis is the only sink of HONO, explain how this mechanism could provide a burst of HO<sub>x</sub> radicals in early morning, and why it would be mainly restricted to environments with very high NO<sub>x</sub>.

### 3. Ozone production efficiency

When ozone production is in the NO<sub>x</sub>-limited regime, an important quantity used to project the benefit of NO<sub>x</sub> emission controls is the ozone production efficiency per unit NO<sub>x</sub> oxidized (OPE). Consider the following simplified mechanism for ozone smog production involving the oxidation of a hydrocarbon (RH) in the presence of NO<sub>x</sub>:



Assume in what follows that (4) is much faster than (2), and that (5) is much slower than (1) and (3). Assume also that all radicals are in steady state. Denote  $k_i$  the rate constant of reaction (i)

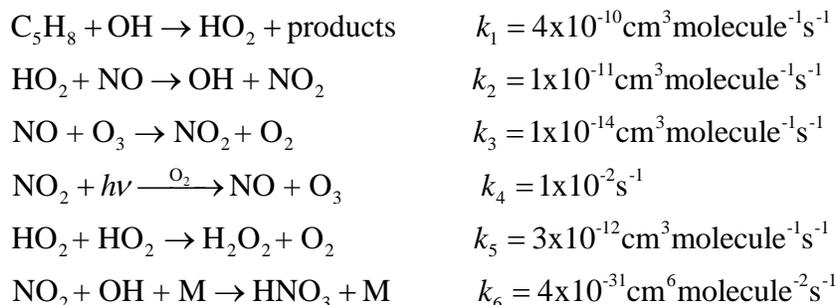
- 3.1 Show that  $\text{OPE} = k_1[\text{RH}]/(k_5[\text{NO}_2])$ .
- 3.2 It is more useful to express the OPE as a function of [NO<sub>x</sub>] rather than as a function of [NO<sub>2</sub>] because of the rapid cycling between NO and NO<sub>2</sub>. Derive an expression for the [NO<sub>2</sub>]/[NO<sub>x</sub>] ratio as a function of [O<sub>3</sub>] only. Replace into your OPE equation. What do you conclude as to the dependence of OPE on the ozone concentration? Explain qualitatively your result. Does this dependence hinder or enhance the effectiveness of NO<sub>x</sub> emission controls for reducing ozone levels?
- 3.3 An alternate branch for reaction (2) produces a stable organic nitrate RONO<sub>2</sub> which is eventually removed by deposition:



Show that if this reaction dominates NO<sub>x</sub> loss (that is, if (2') is much faster than (5)), then the OPE is a constant.

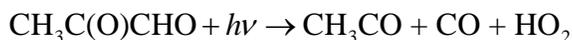
#### 4. Isoprene effect on the ozone production efficiency

Isoprene (C<sub>5</sub>H<sub>8</sub>) emitted from vegetation is an important precursor of ozone in the United States. Consider the following simplified mechanism for oxidation of isoprene in the presence of NO<sub>x</sub>:



and a typical atmosphere for the U.S. in summer containing  $1 \times 10^{10}$  molecules cm<sup>-3</sup> isoprene,  $1 \times 10^{10}$  molecules cm<sup>-3</sup> NO<sub>x</sub>,  $1 \times 10^{12}$  molecules cm<sup>-3</sup> ozone, and  $5 \times 10^8$  molecules cm<sup>-3</sup> HO<sub>2</sub>, with an air density of  $2.5 \times 10^{19}$  molecules cm<sup>-3</sup>. Assume that the “products” of reaction (1) are inert, that all radicals are at steady state, and that the rates of (5) and (6) are slow relative to those of the other reactions.

- 4.1 Calculate the [NO]/[NO<sub>2</sub>] and [HO<sub>2</sub>]/[OH] concentration ratios.
- 4.2 Calculate the rates of the individual reactions and verify that (5) and (6) are indeed slow relative to the others.
- 4.3 For the conditions above, is ozone production in the NO<sub>x</sub>-limited or NO<sub>x</sub>-saturated regime? Briefly explain.
- 4.4 Show that the ozone production efficiency (OPE) per unit NO<sub>x</sub> oxidized is 67 for these conditions. If isoprene emission were to increase, would the OPE increase or decrease? Briefly explain.
- 4.5 In fact the “products” of isoprene oxidation are not inert. One important product is methylglyoxal, CH<sub>3</sub>C(O)CHO, which photolyzes as follows:



Inclusion of this reaction in mechanism (1)-(6) will increase the ozone production rate but not the OPE; briefly explain why.

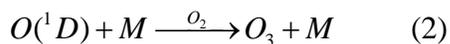
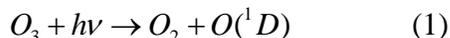
- 4.6 Photolysis of methylglyoxal could actually decrease the OPE by converting NO<sub>x</sub> to PAN; write the corresponding reactions and briefly explain why this would decrease the OPE.

#### 5. A radical chemistry explosion?

Photolysis of formaldehyde (CH<sub>2</sub>O) to produce HO<sub>x</sub> radicals is called a *branching reaction* in the HO<sub>x</sub> catalytic chain because it adds HO<sub>x</sub> radicals as part of the propagation cycle. Such amplification could conceivably lead to an explosive

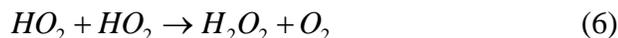
runaway production of HO<sub>x</sub> and we examine here if this can happen in the atmosphere. Throughout this problem, denote  $k_i$  as the rate constant of reaction (i).

- 5.1 The HO<sub>x</sub> radical chain is initiated by the photolysis of ozone in the presence of water vapor:



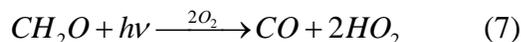
Let  $P(HO_x)$  represent the source of HO<sub>x</sub> radicals from reactions (1)-(3). Express  $P(HO_x)$  as a function of the concentrations of O<sub>3</sub>, H<sub>2</sub>O, and M.

- 5.2 Consider now the following simplified schematic for the subsequent HO<sub>x</sub> propagation and termination steps:



Based on the mechanism (1)-(6), derive an equation for the OH concentration as a function of  $P(HO_x)$ , [CH<sub>4</sub>], and [NO], assuming efficient HO<sub>x</sub> cycling. You should find that OH concentrations increase as [NO] increases and as [CH<sub>4</sub>] decreases.

- 5.3 The effect of methane on HO<sub>x</sub> chemistry is complicated by the photolysis of CH<sub>2</sub>O, producing HO<sub>x</sub> radicals:



Write the HO<sub>x</sub> steady-state equation to include the source from (7), assuming CH<sub>2</sub>O to also be at steady state. Show that this steady-state equation always has a positive solution for [HO<sub>2</sub>], meaning that the system remains stable (no explosion). Show also that under these conditions [OH] is still inversely dependent on [CH<sub>4</sub>] even though (7) provides a source of HO<sub>x</sub>. Explain qualitatively why that is.

- 5.4 Explosive conditions can however arise in the NO<sub>x</sub>-saturated regime, when the loss of HO<sub>x</sub> is not by reaction (6) but instead by reaction of NO<sub>2</sub> with OH:



Write a steady-state equation for HO<sub>x</sub> using (8) instead of (6) as HO<sub>x</sub> sink. Show that the stability of the system depends on the relative abundance of CH<sub>4</sub> and NO<sub>2</sub>.

- 5.5 An alternate sink for CH<sub>2</sub>O is reaction with OH. Without doing any calculations, explain why this alternate sink would help to stabilize HO<sub>x</sub> concentrations in the NO<sub>x</sub>-saturated regime.

## CHAPTER 13: ACID RAIN

### 1. Short questions

- 1.1 A dinosaur extinction theory suggests that massive heating of the Earth's atmosphere in the path of a falling asteroid would have led to extremely acid rain, killing the land vegetation and hence the dinosaurs' food supply. What acid would have been involved?
- 1.2 Nitrate concentrations in rain over the U.S. are observed to be similar in winter and in summer. This observation has been used as evidence for the importance of  $\text{N}_2\text{O}_5$  hydrolysis as a sink of  $\text{NO}_x$  in the troposphere. Briefly explain.
- 1.3 The most abundant organic acids in the atmosphere are formic acid ( $pK_a = 3.8$ ) and acetic acid ( $pK_a = 4.8$ ). On a per mole basis, which of these two acids would most affect the pH of rainwater? Briefly explain.
- 1.4 Liming of lakes by addition of limestone ( $\text{CaCO}_3$ ) is a practical corrective solution to prevent acidification of lakes. Consider a small  $1 \text{ km}^2$  lake receiving  $1 \text{ m}$  precipitation per year with an average pH of 4.5. Show that 1.5 tons of limestone must be dumped into the lake each year to neutralize the acid input. (The atomic weight of calcium is  $40 \text{ g mole}^{-1}$ )

### 2. Sulfuric vs. sulfurous acid

Sulfuric acid produced by oxidation of  $\text{SO}_2$  is a major component of acid rain. However, dissolved  $\text{SO}_2$  is an acid too (sulfurous acid), which may make one wonder about the actual importance of  $\text{SO}_2$  oxidation as a source of acidity. We examine this issue here. The relevant equilibria for  $\text{SO}_2$  dissolution and dissociation in cloudwater are:



- 2.1 Calculate the pH of a droplet of pure water at equilibrium with a typical  $p_{\text{SO}_2} = 1 \times 10^{-8} \text{ atm}$  for a polluted atmosphere. [Hint: ignore  $\text{SO}_3^{2-}$  and  $\text{OH}^-$  in the charge balance calculation, and verify the correctness of this assumption at the end]. You should find a pH value of 4.9. Since the dominant form of sulfur in solution is  $\text{HSO}_3^-$ , conclude as to the effect on pH of oxidizing this sulfur to  $\text{SO}_4^{2-}$ .
- 2.2 A far more important effect has to do with sulfur dissolution. Consider a cloud with a typical liquid water content  $L = 1 \times 10^{-6} \text{ cm}^3$  liquid water per  $\text{cm}^3$  of air and temperature  $T = 280 \text{ K}$ . For a cloudwater pH of 4.9, calculate the fraction of total sulfur in an air parcel that remains in the gas phase as  $\text{SO}_2(\text{g})$  vs. dissolves in the cloudwater phase as  $\text{HSO}_3^-$ . [Hint: you will need to convert the  $\text{SO}_2$  and  $\text{HSO}_3^-$

concentrations to common measures]. You should find that most of the  $\text{SO}_2$  remains in the gas phase.

- 2.3 Oxidation of dissolved  $\text{HSO}_3^-$  to sulfate thus pushes gas-phase sulfur into the aqueous phase, greatly increasing acidity. For the conditions in question 2 and an initial  $p_{\text{SO}_2} = 1 \times 10^{-8}$  atm, calculate the cloudwater pH under conditions where all the sulfur in the air parcel is oxidized to sulfate with no other acids or bases present.

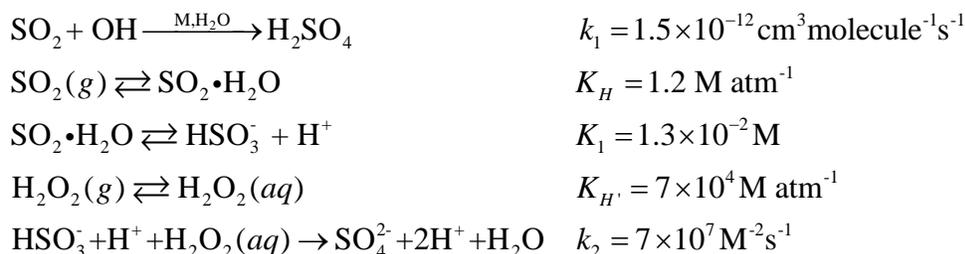
## CHAPTER 14: AEROSOL CHEMISTRY

### 1. Short questions

- 1.1 Reducing ammonia emissions from agriculture is proposed as a way to decrease aerosol nitrate concentrations. Explain briefly the rationale.
- 1.2 It has been argued that decreasing SO<sub>2</sub> emissions to decrease aerosol sulfate could result in an increase in aerosol nitrate, increasing in fact the total aerosol mass concentration. Explain the reasoning.

### 2. Oxidation of SO<sub>2</sub> to sulfate

We show in this problem that in-cloud oxidation by H<sub>2</sub>O<sub>2</sub> is the dominant pathway for SO<sub>2</sub> oxidation and allows for sulfate to be produced within the SO<sub>2</sub> source region. Consider a box model for the U.S. airshed extending 5000 km in the east-west direction and ventilated by a westerly wind of 10 m s<sup>-1</sup>. SO<sub>2</sub> emitted in the airshed can be removed by ventilation, dry deposition ( $k_d = 2 \times 10^{-6} \text{ s}^{-1}$ ), gas-phase oxidation by OH, and in-cloud aqueous-phase oxidation by H<sub>2</sub>O<sub>2</sub>. We examine in this problem the different pathways for SO<sub>2</sub> loss and the consequences for sulfate formation. Assume gas-phase concentrations [OH] = 1 × 10<sup>6</sup> molecules cm<sup>-3</sup> and [H<sub>2</sub>O<sub>2</sub>] = 1 ppb. Further assume  $p = 900 \text{ hPa}$  and  $T = 280 \text{ K}$ . You will need the following information:



- 2.1 Consider first a cloud-free atmosphere, thus ignoring the in-cloud oxidation of SO<sub>2</sub> by H<sub>2</sub>O<sub>2</sub>(aq). Show that the SO<sub>2</sub> lifetime in the U.S. airshed is 2.1 days and that only 27% of emitted SO<sub>2</sub> produces sulfate within the U.S. airshed.
- 2.2 Clouds can greatly speed up the conversion of SO<sub>2</sub> to sulfate through oxidation by H<sub>2</sub>O<sub>2</sub>(aq). Consider a cloudy air parcel with a typical liquid water content  $L = 1 \times 10^{-7} \text{ cm}^3 \text{ water per cm}^3 \text{ air}$ . Show that SO<sub>2</sub> has a lifetime of only 1.7 hours against loss by aqueous-phase reaction with H<sub>2</sub>O<sub>2</sub>(aq) in that air parcel.
- 2.3 Clouds occupy typically 10% of the U.S. airshed, so that the corresponding lifetime of SO<sub>2</sub> in the airshed against in-cloud aqueous-phase oxidation is 17 hours. Show that 81% of the emitted SO<sub>2</sub> is now oxidized to sulfate within the U.S. airshed.
- 2.4 A critical assumption in our calculation is that the H<sub>2</sub>O<sub>2</sub> concentration is not significantly depleted in cloud by oxidation of SO<sub>2</sub>. In the U.S. this assumption is

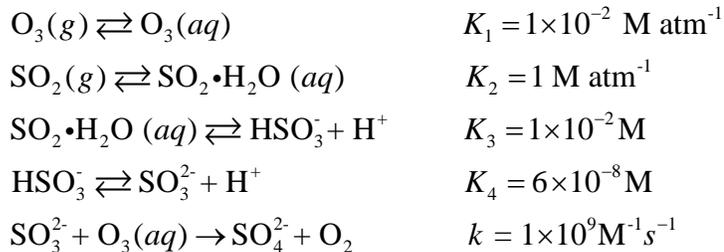
generally acceptable in summer but not in winter. Explain why that would be. [Hint: think of the chemical mechanism for H<sub>2</sub>O<sub>2</sub> production].

- 2.5 A second critical assumption in our calculation is that the SO<sub>2</sub> concentration in the cloud is the same as in the rest of the U.S. airshed. Consider a cloud of typical vertical extent 500 m through which air flows vertically with an updraft velocity (vertical wind)  $w$ . Show that a strong updraft ( $w = 1 \text{ m s}^{-1}$ ) would satisfy the assumption but a weak updraft ( $w = 0.1 \text{ m s}^{-1}$ ) would not.

### 3. Sulfate formation in sea-salt aerosols

The natural source of sulfur in the marine atmosphere is dimethylsulfide (DMS) emitted by phytoplankton. DMS is rapidly oxidized to SO<sub>2</sub>, and the ensuing production of sulfate aerosol has important radiative effects on climate. We examine here the role of sea-salt aerosol in oxidizing SO<sub>2</sub> to sulfate; this process will tend to limit the radiative role of DMS since sea salt is rapidly deposited back to the ocean. Assume throughout the problem that DMS is rapidly and quantitatively oxidized to SO<sub>2</sub> in the marine atmosphere. We focus on the fate of SO<sub>2</sub>.

- 3.1 In most current atmospheric models the sinks for SO<sub>2</sub> in the marine atmosphere are (a) deposition to the ocean, (b) oxidation by H<sub>2</sub>O<sub>2</sub> in clouds, and (c) gas-phase oxidation by OH. Assume that the atmospheric lifetimes for SO<sub>2</sub> against each of these sinks are (a)  $\tau_{dep} = 1 \text{ d}$ , (b)  $\tau_{cloud} = 1 \text{ d}$ , (c)  $\tau_{OH} = 5 \text{ d}$ . Deduce the overall atmospheric lifetime of SO<sub>2</sub> and the fraction that is oxidized in the atmosphere to produce sulfate aerosol.
- 3.2 Oxidation of SO<sub>2</sub> in the MBL can also take place in aqueous sea salt aerosols, with dissolved ozone as oxidant:



Let  $L = 3 \times 10^{-5}$  liters per m<sup>3</sup> air represent the fraction of the MBL volume occupied by sea salt aerosols. Show that the lifetime  $\tau_{salt}$  of SO<sub>2</sub> against oxidation in sea salt aerosols is given by

$$\tau_{salt} = \frac{[\text{H}^+]^2}{LRTkK_1K_2K_3K_4p_{O_3}} \quad (1)$$

where  $p_{O_3}$  is the partial pressure of ozone,  $[\text{H}^+]$  is the aerosol H<sup>+</sup> concentration,  $R$  is the gas constant, and  $T$  is temperature. Explain briefly the dependence on  $[\text{H}^+]^2$ . For typical values of  $p_{O_3} = 40 \times 10^{-9} \text{ atm}$  and  $T = 300 \text{ K}$ , calculate  $\tau_{salt}$  at pH 5 and pH 8.

- 3.3 Sea salt aerosols when emitted have the same  $\text{pH} = 8.2$  as the ocean due to the presence of carbonate ions. Formation of sulfate in these aerosols will cause them to acidify. On the basis of the lifetime  $\tau_{\text{salt}}$  calculated in question (2), show that the potential of sea salt aerosols as sinks for  $\text{SO}_2$  is limited by their alkalinity.
- 3.4 The global source of alkalinity emitted from the ocean as sea salt aerosols is  $3 \times 10^{11} \text{ eq a}^{-1}$ . The global source of DMS is  $20 \text{ Tg S yr}^{-1}$ . Deduce the fraction of DMS-derived  $\text{SO}_2$  that can be oxidized in sea salt aerosols in the marine atmosphere.

#### 4. Aerosol nitrate formation

We examine here the conditions under which atmospheric nitric acid produced by oxidation of  $\text{NO}_x$  is incorporated into the aerosol. Consider an air parcel at  $T = 290 \text{ K}$  containing a fixed gas-phase  $\text{HNO}_3(\text{g})$  concentration of 1 ppbv at 1 atm in equilibrium with an otherwise pure-water aerosol. The relevant equilibria are:



- 4.1 Calculate the pH of the resulting aerosol. You should find  $\text{pH} = 1.3$ . Is aerosol nitrate present mainly as  $\text{NO}_3^-$  or as  $\text{HNO}_3(\text{aq})$ ?
- 4.2 For a typical aerosol liquid water content  $L = 1 \times 10^{-11}$  liter of liquid water per liter of air, calculate the ratio  $(\text{NO}_3^-)/(\text{HNO}_3(\text{g}))$  where ( ) denotes the concentration in moles per liter of air. You should find that that only about 1% of the nitric acid in the air parcel is incorporated into the aerosol.
- 4.3 Explain how the presence of ammonia would facilitate the incorporation of nitric acid into the aerosol phase. What would then be the composition of the resulting aerosol?
- 4.4 A typical cloud has a pH of 5 and a liquid water content  $L = 1 \times 10^{-7} \text{ m}^3$  of liquid water per  $\text{m}^3$  of air. Show that under such cloudy conditions nitric acid is over 99% scavenged by the cloudwater, in contrast to clear-sky conditions where scavenging by aqueous aerosol is negligible.

#### 5. The sulfate-nitrate-ammonium aerosol system

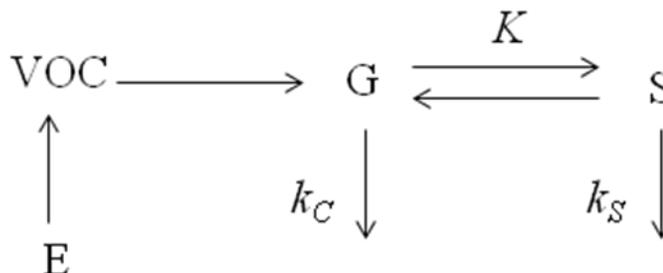
Consider a box model for the US atmosphere including emissions of  $\text{SO}_2$ ,  $\text{NO}_x$ , and  $\text{NH}_3$ . Denote these emissions as  $E_{\text{SO}_2}$ ,  $E_{\text{NO}_x}$ ,  $E_{\text{NH}_3}$  in units of moles per year. Assume that all emitted  $\text{SO}_2$  is converted to sulfate inside the box, that all emitted  $\text{NO}_x$  is converted to  $\text{HNO}_3$  inside the box, that all removal from the box is by deposition, and that all species have the same lifetime against deposition. We consider in that system the formation of ammonium sulfate and nitrate aerosols.

- 5.1 Show that no ammonium nitrate aerosol forms in the system if the emissions satisfy the condition  $E_{\text{NH}_3} < 2 E_{\text{SO}_2}$ .
- 5.2 Show that if  $2E_{\text{SO}_2} + E_{\text{NO}_x} > E_{\text{NH}_3} > 2E_{\text{SO}_2}$  then the formation of ammonium nitrate aerosol is limited by the supply of  $\text{NH}_3$  and not by the supply of  $\text{NO}_x$ .

- 5.3 Under the conditions of 5.2, show that decreasing SO<sub>2</sub> emissions will actually cause an *increase* in aerosol mass concentrations due to formation of aerosol nitrate.

## 6. Formation of secondary organic aerosol

A standard model for organic aerosol formation distinguishes between *primary* organic aerosol (P) directly emitted to the atmosphere from combustion and *secondary* organic aerosol (S) produced in the atmosphere from oxidation of biogenic VOCs followed by dissolution of the oxidation products into the organic aerosol phase. The mechanism for formation of S is described by the following schematic:



Here  $E$  (molecules cm<sup>-3</sup> s<sup>-1</sup>) is the VOC emission rate; VOC oxidation produces a gas-phase species G that partitions in thermodynamic equilibrium with S;  $k_C$  (s<sup>-1</sup>) is the rate constant for gas-phase chemical loss of G; and  $k_S$  (s<sup>-1</sup>) is the rate constant for deposition of S. The thermodynamic equilibrium constant  $K$  (cm<sup>3</sup> molecule<sup>-1</sup>) between G and S is given by

$$K = \frac{[S]}{n_o[G]}$$

where the concentrations in brackets are in units of molecules per cm<sup>3</sup> of air, and  $n_o = [P] + [S]$  is the total concentration of organic aerosol.

- 6.1 Give a brief chemical justification for the presence of  $n_o$  in the denominator of the equilibrium expression. [Hint: use analogy with Henry's law for the equilibrium between a gas and an aqueous aerosol]
- 6.2 Assuming steady state for the concentrations of VOC, G, and S, write a quadratic equation for [S] as a function of  $E$ ,  $k_C$ ,  $k_S$ ,  $K$ , and [P].
- 6.3 Calculate [S] for the two limits [P]  $\rightarrow \infty$  (highly polluted conditions) and [P] = 0 (pristine conditions). Does the "biogenic" secondary organic aerosol S actually include an anthropogenic enhancement from combustion?
- 6.4 You should have found in the previous question that S does not form at all in the limit [P] = 0 if  $k_C > KE$ . Explain this threshold in terms of the saturation vapor pressure of G.

## 7. Glyoxal as a source of organic aerosol

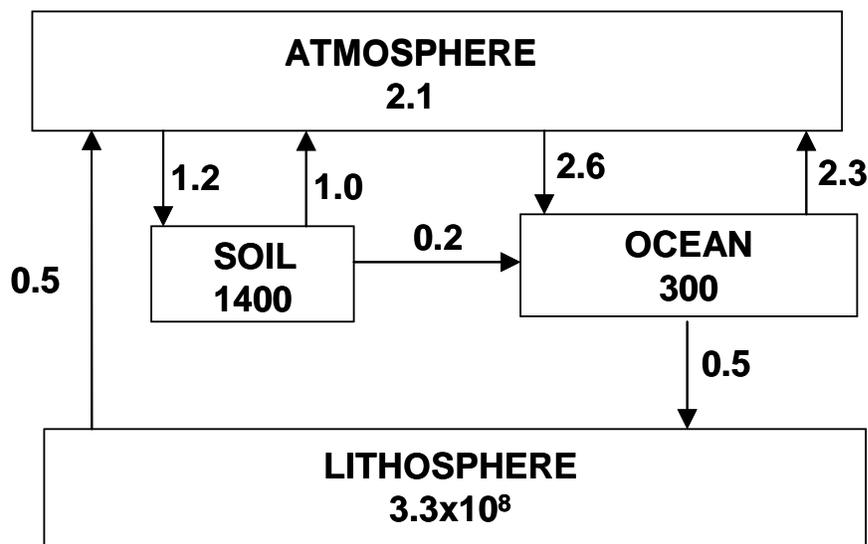
Glyoxal (CHOCHO) is produced in the atmosphere by oxidation of isoprene. It has been proposed as an important source of organic aerosol. We examine here its potential importance in the United States.

- 7.1 Glyoxal has mean atmospheric lifetimes of 2 hours against photolysis, 8 hours against oxidation by OH, and 8 hours against uptake by aqueous particles to form aerosol. What fraction of atmospheric glyoxal will form aerosol?
- 7.2 Isoprene emission in the U.S. in summer is estimated to be  $5 \times 10^{11}$  molecules  $\text{cm}^{-2} \text{s}^{-1}$ . The glyoxal molar yield from isoprene oxidation is 10%. Assume a mixing depth of 1 km and an aerosol lifetime of 3 days, and further assume that glyoxal is in steady state. Calculate the resulting mean concentration of organic aerosol (in units of  $\mu\text{g carbon m}^{-3}$ ) from the glyoxal formation pathway. Compare to typical U.S. observations of  $2 \mu\text{g C m}^{-3}$  for the concentration of organic aerosol.

# CHAPTER 15: MERCURY IN THE ENVIRONMENT

## 1. Global geochemical cycle of mercury

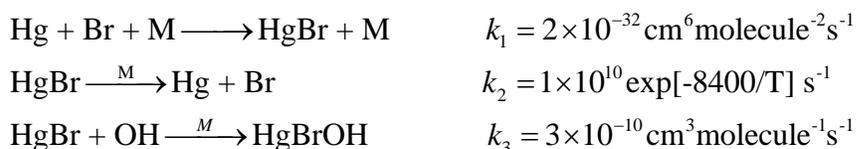
The diagram below shows an estimate of the natural steady-state global geochemical cycle of mercury. Inventories are in Gg and rates are in  $\text{Gg a}^{-1}$ .



- 1.1 Calculate the lifetime of mercury in each reservoir.
- 1.2 Anthropogenic activity (mainly fossil fuel combustion and mining) has disturbed the natural mercury cycle, transferring additional mercury from the lithosphere to the atmosphere. Calculate the characteristic time for return of this mercury to the lithosphere.
- 1.3 This anthropogenic emission amounts to 200 Gg over the past 200 years. On the basis of your answers to questions (1) and (3), show that one may assume this anthropogenic mercury to have remained in the atmosphere/soil/ocean system and to be roughly at equilibrium between these three reservoirs. Conclude as to the % increases of mercury in the soil and ocean reservoirs as a result of human influence.

## 2. Mercury oxidation by Br atoms

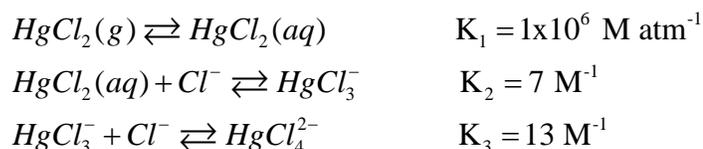
Oxidation by Br atoms has been proposed as an important pathway for oxidation of  $\text{Hg}(0)$  to  $\text{Hg}(\text{II})$ . We examine the rate of this process in surface air ( $p = 1000$  hPa,  $T = 298$  K) and in the upper troposphere ( $p = 200$  hPa,  $T = 200$  K). Assume in what follows a Br atom concentration  $[\text{Br}] = 1 \times 10^5$  molecules  $\text{cm}^{-3}$  in surface air and  $[\text{Br}] = 1 \times 10^6$  molecules  $\text{cm}^{-3}$  in the upper troposphere (technically it should be 'atoms', not 'molecules', but we use 'molecules' for unit consistency), and a uniform OH concentration  $[\text{OH}] = 1 \times 10^6$  molecules  $\text{cm}^{-3}$ . Consider the mechanism



- 2.1 Calculate the lifetimes of HgBr in surface air and in the upper troposphere. Identify the dominant HgBr loss pathway in each case.
- 2.2 Assuming steady state for HgBr, calculate the lifetime of Hg(0) against conversion to Hg(II) in surface air and in the upper troposphere. Conclude as to the potential importance of this mechanism for the global mercury cycle.

### 3. Mercury deposition to the ocean

Mercury deposition to the ocean has been postulated to involve atmospheric oxidation of Hg(0) to Hg(II) in the atmosphere followed by uptake of Hg(II) by aqueous (aq) sea-salt particles and deposition of these particles. We examine here the plausibility of this mechanism. Hg(II) in the marine atmosphere is thought to be mainly present as HgCl<sub>2</sub>. Uptake by sea-salt particles proceeds by the following equilibria:



Consider a typical marine atmosphere with relative humidity of 90% and a dry sea salt concentration of 10 μg per m<sup>3</sup> of air. Assume that this sea salt is pure NaCl with solubility constant in water  $K_s = [\text{Na}^+][\text{Cl}^-] = 36 \text{ M}^2$ .

- 3.1 Show that the sea salt particles are aqueous and that [Cl<sup>-</sup>] = 3 M. [Hint: assume that the particle is mainly water so that the water concentration in the particle is 55 M, and check that the constraint from the solubility constant is satisfied]
- 3.2 Show that the liquid water content of the sea salt aerosol is  $L = 3 \times 10^{-11} \text{ m}^3$  of water per m<sup>3</sup> of air. Use for this calculation  $M_{\text{NaCl}} = 59 \text{ g mol}^{-1}$ .
- 3.3 Calculate the fraction of total atmospheric Hg(II) that is incorporated in the sea-salt aerosol. Assume for this calculation  $T = 300 \text{ K}$ .
- 3.4 Would this fraction increase or decrease if the relative humidity rises to 95%? Briefly explain.