

INTRODUCTION TO ATMOSPHERIC CHEMISTRY: SUPPLEMENTAL QUESTIONS AND PROBLEMS

13th EDITION

by Daniel J. Jacob
Harvard University
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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 course segments on aerosol chemistry and on mercury. I have included problems to support these course segments. All problems are from recent exams in my course.

This 13th edition includes several new problems and questions, and a few corrections to the previous edition.

The problems are aimed at the advanced undergraduate and beginning graduate 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 building intuition and promoting understanding of processes, and it trains students in the important art of doing back-of-the-envelope calculations. 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. To obtain the solutions, send me an email certifying your instructor status. Reference to a university department website is generally sufficient.

I want to thank Colette Heald (MIT), Randall Martin (Dalhousie), Gabriele Curci (U. L'Aquila), Amos Tai (CUHK), Jennifer Murphy (U. Toronto), Arlene Fiore (Columbia), Dylan Millet (U. Minnesota) 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.

Daniel J. Jacob
Harvard University
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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 Does it make sense to report aerosol concentrations as mixing ratios?
- 1.4 We derived from the phase rule that the gas-liquid equilibrium of pure water has only one degree of freedom ($c = 1$ and $p = 2$ imply $n = 1$), explaining why $p_{H_2O,SAT}$ depends only on T . However, the actual atmosphere contains many chemical species other than water. Consider the $H_2O-N_2-O_2$ system; here we have $c = 3$ and therefore from the phase rule $n = 3$. This implies that in the $H_2O-N_2-O_2$ system there are three independent variables controlling the equilibrium state between the gas and a pure water phase. Is this inconsistent with our previous result that $p_{H_2O,SAT}$ depends only on T ?
- 1.5 In an atmosphere with fixed mixing ratio of water vapor, what two processes can cause an increase in relative humidity?
- 1.6 We saw that a cloud in the atmosphere can remain liquid down to temperatures well below freezing. 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?
- 1.7 At a given temperature, how does evaporation of water from the ocean depend on ocean salinity?
- 1.8 What is the relative increase in surface area of a water-soluble particle as the relative humidity increases from 50% to 90%, assuming the same volume per mole for water and solute? What is the resulting percentage decrease in visibility?
- 1.9 What happens to that particle when the relative humidity reaches exactly 100%?

2. Seeing your breath

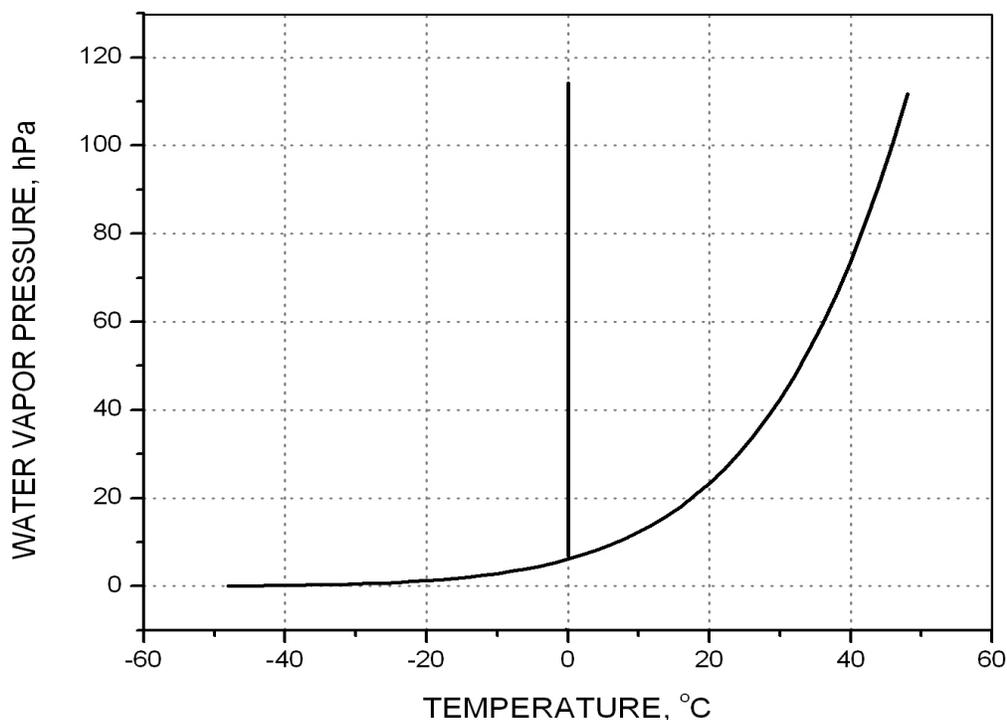
On cold mornings you can see your breath – let's figure out why. Consider the phase diagram of water below [Note that it looks different from the one in the book because it uses a linear scale for p_{H_2O}]. Your breath is at 37°C and 90% relative humidity when it leaves your mouth (call this point A 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

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$$T = fT_B + (1-f)T_A$$

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

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.



3. Wet and dry mixing ratios

One has to be careful with the general statement that mixing ratios are conserved during transport.

- 3.1 Consider an air parcel at sea level ($p = 1013$ hPa) with 30°C and 50% RH. The saturation water vapor pressure at 30°C is 42 hPa. Show that the water mixing ratio in this air parcel is $C_{H_2O} = 0.021$ mol mol⁻¹.
- 3.2 Assume a CO₂ mixing ratio of 410 ppm in that sea-level air parcel. As the air parcel rises through the air, its water vapor may be removed by cloud formation and precipitation. Assuming 100% removal of water vapor, and no dissolution of CO₂ in the condensed water, what is the mixing ratio of CO₂ in the dried-out air parcel?

- 3.3 A way to ensure that mixing ratio is conserved during transport is to define it relative to dry air, so $C_X = \text{moles of X}/(\text{mole of dry air})$ where “dry air” excludes the contribution from water vapor. Briefly explain.

CHAPTER 2: ATMOSPHERIC PRESSURE

1. Short questions

- 1.1 Mercury is toxic and expensive! How about replacing mercury by water in the mercury barometer instrument? How long a tube would we need? (the density of mercury is 13.6 g cm^{-3})
- 1.2 The Badwater Ultramarathon held every July 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?
- 1.3 Why does it take longer to boil an egg in Denver than in Boston?

2. Measuring aerosol concentrations

Aerosol particle concentrations are conventionally reported in units of $[\mu\text{g m}^{-3}]$ but this is awkward for interpreting vertical aerosol profile measurements from aircraft.

- 2.1 Aerosol concentrations measured in units of $[\mu\text{g m}^{-3}]$ decrease with altitude even in a well-mixed atmosphere. Assuming an atmosphere where aerosols are well-mixed vertically and using the barometric law with scale height of 7.4 km, calculate the % decrease in aerosol concentration $[\mu\text{g m}^{-3}]$ from the surface to 1 km altitude. You should find a 13% decrease.
- 2.2 An alternative approach used in aircraft measurements is to report aerosol concentrations in units of $[\mu\text{g sm}^{-3}]$, where sm is a “standard cubic meter” of air at standard conditions of temperature and pressure (STP): 1 atm and 273 K. Show that if the aerosols are well-mixed vertically then the concentration measured in units of $[\text{g sm}^{-3}]$ is uniform with altitude. [*Hint: show that $[\text{g sm}^{-3}]$ is actually a mixing ratio unit*].

3. The Venusian atmosphere

Consider the following data for Venus and Earth:

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

- 3.1 How does the total mass of the Venusian atmosphere compare to that of Earth?

- 3.2 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)
- 3.3 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?

4. Gravitational separation of air

N_2 and O_2 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_2/O_2 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_2/O_2 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.

- 4.1 Estimate the altitude at which gravitational separation becomes important in the atmosphere, as indicated by D and K being of same order of magnitude ($D/K \sim 1$)
- 4.2 Calculate the resulting maximum possible percentage increase in the N_2/O_2 ratio per 10 km increase in altitude, assuming a temperature of 200 K.

5. An oxygen source in the Archean atmosphere

Photolysis of water vapor releases oxygen atoms that eventually form O_2 , providing a source of O_2 to the atmosphere. Presently this source is negligibly small. It could have been much more important in the Archean (2.5-4 billion years ago), resulting in significant levels of O_2 prior to the onset of photosynthesis. Here we examine this hypothesis.

- 5.1 Photolysis of water vapor in the present-day atmosphere only takes place in the upper atmosphere above 40 km altitude, where the water vapor concentration is very low. The bottleneck for transporting water vapor from the surface to the upper atmosphere is the vertical crossing of the tropopause, which takes place in the tropics. Consider an air parcel saturated with respect to ice at the tropical tropopause at $z = 16 \text{ km}$ and $T = 195 \text{ K}$, corresponding to $P_{H_2O,SAT} = 0.076 \text{ Pa}$. Assuming a scale height $H = 7.4 \text{ km}$ for the atmosphere, calculate the water vapor mixing ratio in that air parcel. You should find $C_{H_2O} = 6.6 \text{ ppm}$. Compare to a typical water vapor mixing ratio $C_{H_2O} = 1000 \text{ ppm}$ in surface air. Why is there such a large decrease in water vapor mixing ratio between the surface and the tropopause?
- 5.2 Once the air parcel has made it through the tropopause it will eventually (slowly) reach the upper atmosphere with no further decrease in water vapor mixing ratio. Explain why there is no decrease in C_{H_2O} as the air parcel is transported from the tropopause up to 40 km altitude.

- 5.3 The O_2 source from water vapor photolysis could have been much higher in the Archean than today in part because of higher surface temperatures and in part because water vapor would have photolyzed at lower altitudes in the absence of a UV shield. Consider a surface temperature of 330 K for the Archean and the same mean lapse rate as today; determine the saturation water vapor pressure at 10 km altitude (read it off the water phase diagram from Chapter 1). Assuming that the source of O_2 from water vapor photolysis in the Archean was limited by $P_{H_2O,SAT}$ at 10 km altitude, estimate how much larger the O_2 source from H_2O photolysis would have been in the Archean relative to today.

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 CO₂ by the biosphere, (b) Photolysis of gases.
- 1.2 An elementary reaction $A+B \rightarrow \text{products}$ has rate law $-d[A]/dt = k[A][B]$, but that does not necessarily mean that the loss rate of A is proportional to the concentration of A (first-order loss). Explain. Under what limiting conditions is the loss rate proportional to [A]? Under what limiting conditions is it independent of [A]?
- 1.3 The Montreal Protocol to protect the ozone layer banned worldwide production of the chlorofluorocarbon CFC-12 in 1996. 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?
- 1.4 Consider a pollutant emitted in an urban airshed of 100 km dimension. The pollutant can be removed from the airshed by oxidation, precipitation scavenging, or export. The lifetime against oxidation is 1 day. It rains once a week. The wind is 20 km/h. Which is the dominant pathway for removal?
- 1.5 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). Air exchanges between the troposphere and the stratosphere. If the residence time of air in the stratosphere is 2 years, what is the residence time of air in the troposphere?
- 1.6 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 CO₂ concentrations be explained by the known rate of CO₂ 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. Atmospheric helium

Helium is produced by decay of radioactive elements in the solid Earth and is emitted to the atmosphere by seeps and vents. The only atmospheric sink of helium is escape to outer space, with a lifetime of 1 million years. The atmospheric concentration of helium is 5.2 ppm. The atmosphere contains 1.8×10^{20} moles of air.

- 2.1 Assuming steady-state between emission of helium to the atmosphere and escape to outer space, calculate the helium emission rate in units of $[\text{mol a}^{-1}]$ (moles per year). You should find a value of $9.4 \times 10^8 \text{ mol a}^{-1}$.
- 2.2 Over the past century, helium has been actively mined from the Earth for use in industry and in balloons. The current production rate of helium from mining is $8 \times 10^9 \text{ mol yr}^{-1}$. All of the mined helium is eventually emitted to the atmosphere, and assume that there is no time lag between mining and emission. At this mining rate, how long would it take for the atmospheric helium concentration to increase by 1%? [Hint: assume that escape to space is negligible over the time period needed to increase helium by 1%, and verify this assumption using your answer at the end].

3. Observing the net US source of CO₂

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^{-1} . The air density in this column is taken to be $n_a = 2 \times 10^{19} \text{ molecules cm}^{-3}$. The US fossil fuel source of CO₂ is 2.0 Pg C a^{-1} and we assume it to be evenly distributed over the contiguous US surface area of $7 \times 10^6 \text{ km}^2$. Assuming no other source or sink of CO₂ in the US, calculate the resulting increase of CO₂ mixing ratio from the west coast to the east coast. With CO₂ 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 CO₂ in the US. is offsetting fossil fuel emission?

4. Verifying emission controls

Consider a box model for the atmosphere over the contiguous US of length L [km] in the east-west direction, ventilated by a steady westerly wind of speed U [km h^{-1}]. A pollutant X is emitted in the box at a rate E [$\text{kg m}^{-3} \text{ s}^{-1}$]. The pollutant has a lifetime τ [h] against oxidation and no loss by deposition.

- 4.1 For numerical values $L = 4,000 \text{ km}$, $U = 10 \text{ km h}^{-1}$, $\tau = 100 \text{ h}$, what is the dominant loss process for the pollutant X in the US box?
- 4.2 Assuming a zero concentration of X in the background air blowing into the US, show that the steady-state equation for the concentration $[X]$ [kg m^{-3}] of the pollutant inside the US box is given by

$$[X] = \frac{E}{\frac{U}{L} + \frac{1}{\tau}}$$

- 4.3 The Environmental Protection Agency (EPA) says that it has been working hard to control the emissions of X and claims that US emissions have been decreasing at a rate of 10% per year. But atmospheric measurements of the concentration of X

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show a decrease of only 5% per year. On the basis of the above equation, explain how these atmospheric measurements suggest that EPA has been exaggerating the success of its emission controls.

- 4.4 Another possible explanation, however, is that the concentration of X in the background air blowing into the US may not be negligible. Modify your steady-state equation for [X] to include a non-zero background $[X]_b$ for the air blowing into the US. From this equation, explain qualitatively why the non-zero background will result in a relative atmospheric decrease of [X] [% per year] that is less than the relative decrease of emissions. Also explain qualitatively why this background effect would become increasingly important as emissions decrease.

5. 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.

- 5.1 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.
- 5.2 Calculate the time-averaged aerosol mass over that period.
- 5.3 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?

6. Ventilation of the eastern US

- 6.1 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 (kg d⁻¹) and a first-order chemical loss rate constant k (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.
- 6.2 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 $k \rightarrow \infty$].

7. 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 $-d[X_i]/dt = k_i[X_i][OH]$ 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 (s^{-1}). Assume that the hydrocarbons have no other sources and that background concentrations are negligible.

- 7.1 Show that the mixing ratio C_1 of hydrocarbon X_1 measured at the observation site is given by

$$C_1 = C_{1,o} \exp\left[\frac{-(k_1[\text{OH}] + k_d)x}{U}\right] \quad (1)$$

where $C_{1,o}$ is the concentration at the source and $[\text{OH}]$ is in units of molecules cm^{-3} .

- 7.2 Equation (1) could in principle be used to infer $[\text{OH}]$, but a practical problem is that $C_{1,o}$ 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

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

- 7.3 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.
- 7.4 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?

8. Fossil fuel combustion as a source of water vapor

Current global CO_2 emission from fossil fuel combustion is 7 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.

- 8.1 Write the stoichiometric reaction for the oxidation of $\text{CH}_{1.6}$ by oxygen during combustion.
- 8.2 Knowing that the global precipitation rate is 3 mm d^{-1} , calculate the global source (Pg a^{-1}) of water vapor to the atmosphere. Compare to the source of water vapor from fossil fuel combustion.
- 8.3 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 (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.

9. Inferring atmospheric lifetimes from observed seasonal variations

Consider a box model for a tropical region with a constant biomass burning source for 3 months out of the year (January-March) and no biomass burning in the other 9 months. Consider a species emitted at a rate E (kg month^{-1}) during the biomass burning season and zero outside that season. Assume for this species a constant lifetime τ for removal from the atmosphere. Let $m(t)$ be the mass of the species in the box at time t .

- 9.1 Write equations relating $m(t)$ to E and τ during the biomass burning season and outside of the biomass burning season. Draw a qualitative plot of the seasonal variation of $m(t)$.
- 9.2 Give an expression for the ratio of the seasonal maximum to seasonal minimum value of $m(t)$ as a function of τ . We call this the *relative seasonal amplitude*.
- 9.3 Measurements of the relative seasonal amplitude provide empirical constraints on the lifetimes of atmospheric gases. Consider for example hydrogen cyanide (HCN), a species emitted solely by biomass burning. Atmospheric observations show a relative seasonal amplitude of 3 for HCN. Show that this implies an HCN atmospheric lifetime of 8 months in our box model.
- 9.4 It is thought that the sink for atmospheric HCN is uptake by the ocean followed by microbial consumption in the ocean. HCN dissolves in the ocean with a Henry's law constant $K_H = 12 \text{ M atm}^{-1}$. Calculate the equilibrium fractionation $F = N_{\text{HCN(g)}} / (N_{\text{HCN(g)}} + N_{\text{HCN(aq)}})$ between the atmosphere and the surface ocean (volume $V = 4 \times 10^{16} \text{ m}^3$), where $N_{\text{HCN(g)}}$ is the total number of moles of HCN in the atmosphere and $N_{\text{HCN(aq)}}$ is the total number of moles of HCN in the surface ocean. You should find $F = 0.27$.
- 9.5 Assuming equilibrium between the atmosphere and the surface ocean, and no transfer from the surface ocean to the deep ocean, what lifetime of HCN in the

surface ocean against microbial consumption is needed to explain an 8-month atmospheric lifetime of HCN?

10. Beryllium isotopes as tracers of vertical transport

The radioactive beryllium isotope ^7Be is commonly used as a tracer of air of high-altitude origin. ^7Be is produced by cosmic rays at high altitude. It has no other source. The global ^7Be source is 150 g a^{-1} , of which $2/3$ is in the stratosphere and $1/3$ is in the upper troposphere. ^7Be attaches immediately to aerosols and is removed by aerosol wet deposition. It is also lost by radioactive decay with a corresponding lifetime of 77 days. Consider for this problem a two-box model for the troposphere-stratosphere system where the tropospheric box (T) extends from 1000 to 150 hPa and the stratospheric box (S) extends from 150 to 1 hPa. Air exchange between these two boxes is described by first-order transfer rate constants. Assume that ^7Be is in steady state.

- 10.1 Calculate the total mass of ^7Be in the stratosphere, assuming that you can neglect transfer to the troposphere as a sink (we will verify this assumption below). You should get a value of 21 g.
- 10.2 Observations indicate a total mass of ^7Be in the troposphere of 3.0 g and a loss rate from deposition of 0.14 g d^{-1} . Calculate the lifetime of ^7Be in the troposphere against deposition. This value is fairly long relative to the typical weekly frequency of precipitation. Explain qualitatively why.
- 10.3 Write a steady-state mass balance equation for tropospheric ^7Be . Calculate from that equation the residence time of air in the stratosphere against downward transport to the troposphere. You should find a value of 1.3 years. Justify from this result the assumption made in question 4.1.
- 10.4 What fraction of tropospheric ^7Be mass is produced in the stratosphere? Based on this result, would you expect high- ^7Be events measured in surface air to be more sensitive to the influence of downward transport from the upper troposphere or from the stratosphere?
- 10.5 Another radioactive isotope of beryllium is ^{10}Be , which has the same vertical source distribution as ^7Be but a much longer lifetime against radioactive decay (2 million years). ^{10}Be is a much better tracer of events of stratospheric influence on surface air than ^7Be . Explain qualitatively why.

11. Atmospheric titration.

Consider two chemicals A and B with atmospheric masses m_A and m_B [kg] and constant emissions E_A and E_B [kg s⁻¹], reacting with each other in the atmosphere by

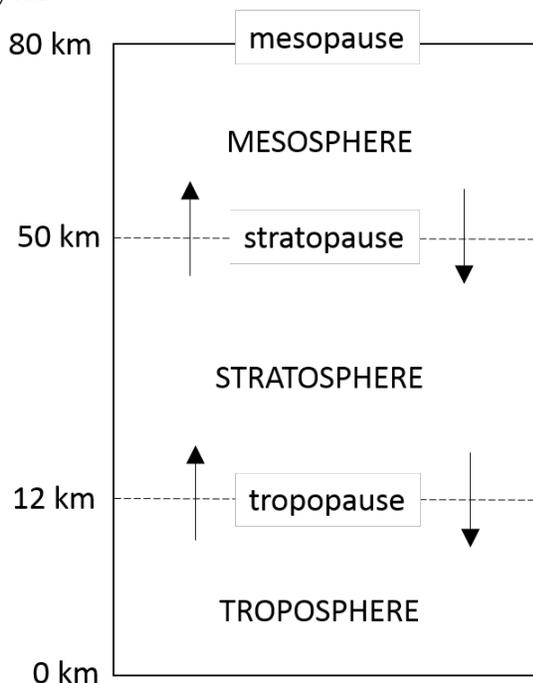


where k is a rate constant with units of [kg⁻¹ s⁻¹]. Assume initial conditions $m_A(0) = m_B(0) = 0$.

- 11.1 Write mass balance equations for m_A and m_B in a 1-box model with emissions and the above reaction as the only terms. Use these equations in what follows.
- 11.2 For the special case $E_A = E_B = E$, show that the steady-state solution is $m_A = m_B = (E/k)^{1/2}$ [Hint: in that special case we necessarily have $m_A = m_B$]
- 11.3 Consider now the general case where the emissions are different: $E_A > E_B$. In that general case there is no steady-state solution for A, but show that B still has a steady-state solution $m_B = E_B/(kt(E_A - E_B))$. Such a solution is often called “quasi-steady state” because it varies with time, whereas “steady state” is generally viewed as time-invariant. Explain the difference.

12. Exchange between the troposphere and the mesosphere

Consider a 3-box model for the atmosphere separating the troposphere, the stratosphere, and the mesosphere (see Figure). Altitudes are relative to sea level. Air in the stratosphere has a residence time of 2 years and air in the mesosphere has a residence time of 1 year.



- 12.1 Using a scale height of 7.4 km and a surface pressure of 1000 hPa, calculate the pressures at the tropopause, stratopause, and mesopause.
- 12.2 Calculate the residence time of air in the stratosphere against transport to the mesosphere based on mesosphere-stratosphere mass balance. Conclude that the flow of air out of the stratosphere is almost entirely to the troposphere, and from there deduce the residence time of air in the troposphere.
- 12.3 Calculate the average time for a molecule of air in the troposphere to be transported to the mesosphere. You should find a value of about 700 years. [*Hint: once a molecule of air from the troposphere is transported to the stratosphere, it can either be transported to the mesosphere or return to the troposphere. Calculate the fraction that is transported to the mesosphere*].
- 12.4 The CO₂ concentration in surface air is 400 ppb for present day, as compared to 280 ppb for the pre-industrial atmosphere. Assuming that CO₂ is chemically inert, would you expect the present-day CO₂ concentration in the mesosphere to be closer to 400 ppb or to 280 ppb?

13. Observing methane emission from space

We wish to use satellite measurements of methane to detect leaky natural gas production facilities. The satellite measures the column mixing ratio of methane X defined as

$$X = \frac{\Omega}{\Omega_a}$$

where Ω is the column concentration of methane [molecules CH₄ cm⁻²] and Ω_a is the column concentration of air [molecules air cm⁻²]. The measurements are horizontal averages over square observation pixels of side L [km].

- 13.1 Consider an isolated leaky facility with emission E [kg CH₄ h⁻¹] and no surrounding methane emissions. Show that the increase ΔX in the column mixing ratio detected by the satellite for that pixel relative to upwind is

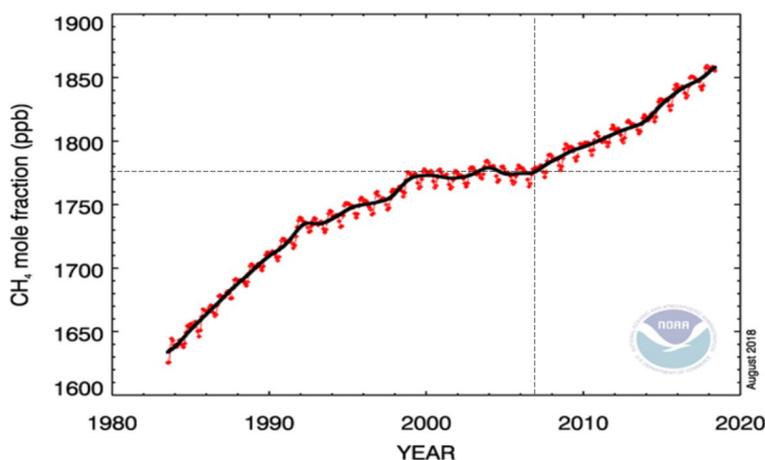
$$\Delta X = \frac{M_a}{M} \frac{Eg}{ULp}$$

where M_a and M are the molecular weights of air and methane, g is the acceleration of gravity, U is the wind speed, and p is the surface pressure.

- 13.2 A typical leaky facility emits $E = 1000$ kg CH₄ h⁻¹. Your satellite has a pixel size $L = 4$ km. The background methane concentration is 1800 ppb. Using your own estimate of a typical wind speed, calculate the % precision required for the satellite to be able to detect the leaky well. You should find a value of the order of 0.1%. This is a difficult measurement! As the equation shows, a finer pixel size would provide better detectability. Explain qualitatively why that is the case.

14. Growth of atmospheric methane

Atmospheric methane is a major greenhouse gas emitted by both natural and anthropogenic sources. It is removed from the atmosphere by oxidation with a first-order rate constant $k = 0.1 \text{ a}^{-1}$. There are no other sinks.



- 14.1 The Figure above shows observed trends of global mean methane mixing ratios. We see from the Figure that methane grew in the 1990s but then leveled off in the early 2000s to a stable mixing ratio of $C_{2007} = 1775 \text{ ppb}$. Explain briefly how this evolution is consistent with methane achieving a steady state between emission and oxidation.
- 14.2 But in 2007 growth started again abruptly. Let $m(0)$ and $E(0)$ represent the mass and emission of methane in 2007, when methane is assumed to be in steady state. From 2007 on the data show that methane increased by $0.3\% \text{ yr}^{-1}$, which we can write as $m(t) = m(0)(1 + \alpha t)$ where $\alpha = 3 \times 10^{-3} \text{ a}^{-1}$ and t is time in years after 2007. Assuming that k has remained constant, and using the mass balance equation, show that the emission rate has been increasing as

$$E(t) = E(0)\left(1 + \frac{\alpha}{k} + \alpha t\right)$$

- 14.3 In this expression there is a step jump in emissions in 2007 by $E(0)\alpha/k$, and a sustained growth in emissions $E(0)\alpha t$. Briefly explain why both are necessary to explain the observed methane growth after 2007.

CHAPTER 4: ATMOSPHERIC TRANSPORT

1. Short questions

- 1.1 Would you expect winds to be generally stronger in winter or in summer?
- 1.2 The Coriolis force responsible for anticyclonic and cyclonic motions (rotation around Highs and Lows) applies only when viewing motions from the perspective of the rotating Earth. Why then do we see rotating hurricanes (strong cyclones) in images from weather satellites out in space?
- 1.3 What happens to tropical cyclones when they cross the Equator? Do they start turning the other way?
- 1.4 Air quality agencies in the US are more concerned about transport of pollution from Asia than from Europe, even though Europe is closer. Explain briefly why on the basis of the prevailing atmospheric circulation.
- 1.5 Based on the seasonal sloshing of the ITCZ between the northern and southern tropics, at what time of year would you expect CO₂ emitted in the northern hemisphere to be transferred to the southern hemisphere?
- 1.6 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?”, Jack brushes him off - “It’s sinking too fast. It doesn’t have time”. Can Jack be right?
- 1.7 Fairbanks in central Alaska has a serious air pollution problem in winter because of suppressed ventilation. Explain briefly why that would be.
- 1.8 A sea-breeze circulation often produces a temperature inversion. Explain why.
- 1.9 A well known air pollution problem is “fumigation” where areas downwind of a power plant with tall stacks experience sudden bursts of very high pollutant concentrations in mid-morning. Can you explain this observation on the basis of the diurnal variation of atmospheric stability?
- 1.10 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.
- 1.11 A persistent mystery in atmospheric chemistry is why the stratosphere is so dry (3-5 ppmv H₂O). 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.
- 1.12 Wildfires often trigger thunderstorms. Why?
- 1.13 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?

- 1.14 A tower measures vertical fluxes of CO₂ 10 m above the top of a forest canopy. For a typical horizontal wind speed of 10 m s⁻¹ 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 CO₂ 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 $H = 7.4 \text{ km}$, 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 $\Gamma_w = 6.5 \text{ K km}^{-1}$, 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 $H = 7.4 \text{ km}$*].
- 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^{-1} , and cloudwater in the updraft is converted to precipitation with a rate constant $k = 5 \times 10^{-3} \text{ s}^{-1}$. 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 $z = 5.6 \text{ km}$. 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

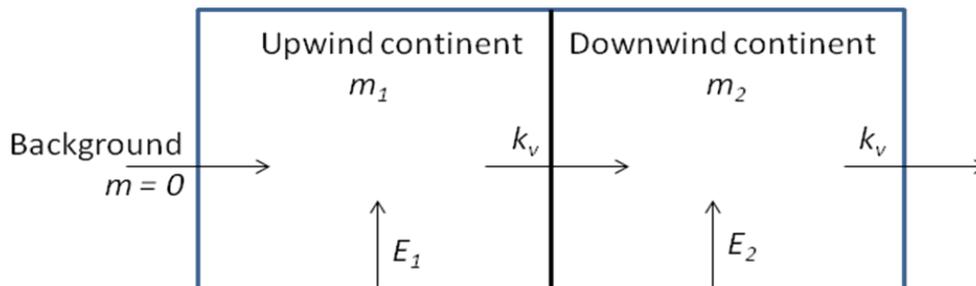
$$C = \frac{C_o h_o}{h_o + at} \exp[-kt] + \frac{aC'}{k(h_o + at)} (1 - \exp[-kt])$$

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 (kg s^{-1}), and with a first-order loss rate constant for chemical loss k_C (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 N₂ reservoir. In fact, denitrification is essential for maintaining life in the interior of continents. Why?
- 1.2 Mars has a very thin atmosphere dominated by CO₂. N₂ accounts for only 2.6% of the Martian atmosphere. Why is there so little N₂ on Mars, as compared to Earth?
- 1.3 In the absence of denitrification, nitrogen would eventually end up as nitrate in the deep ocean. Based on our box model of the nitrogen cycle, what is the lifetime of atmospheric N₂ against transfer to the deep ocean?
- 1.4 Although volcanoes don't emit O₂ they do emit a lot of oxygen (as H₂O and CO₂). Both H₂O and CO₂ photolyze in the upper atmosphere. Photolysis of H₂O results in production of atmospheric O₂ but photolysis of CO₂ does not. Why this difference?
- 1.5 The present-day rate of accumulation of atmospheric CO₂ is about 50% of the rate of emission from fossil fuel combustion. Does this mean that atmospheric CO₂ has a lifetime of only about 2 years, since 50% of the emission gets removed in one year?
- 1.6 The present-day rate of accumulation of atmospheric CO₂ is about 50% of the rate of emission from fossil fuel combustion. Assuming that the deposition rate stays constant, by what fraction would we need to decrease emissions in order to get CO₂ concentrations to decrease?
- 1.7 A famous politician suggested sarcastically that “we all quit breathing” to reduce the source of CO₂ to the atmosphere. Would that work? Briefly explain.
- 1.8 Dead organisms sedimenting on the ocean floor have calcium carbonate (CaCO₃) shells. Does the burial of the oxygen in these shells affect atmospheric oxygen?
- 1.9 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 CO₂?
- 1.10 As oceans acidify due to increasing CO₂, it will become more difficult for marine organisms to produce calcium carbonate shells. Briefly explain why.
- 1.11 The present-day fossil fuel source of CO₂ to the atmosphere is 8 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 3x10¹⁴ m². The present-day CO₃²⁻ concentration in the surface ocean is 2x10⁻⁴ M. What fraction of that CO₃²⁻ is consumed in a single year of fossil fuel input?
- 1.12 Melting of polar icecaps decreases deep water formation and hence the transfer of CO₂ to the deep ocean. Explain why, and how this represents a positive feedback to climate change.
- 1.13 It is proposed to reduce CO₂ emissions by asking farmers to compost rather than burn their agricultural waste. Does this make sense?

- 1.14 From the standpoint of controlling atmospheric CO₂, is it better to heat your home with a wood stove or by natural gas?
- 1.15 Above-ground nuclear tests in the 1950s injected large amounts of ¹⁴CO₂ in the atmosphere, but atmospheric observations following the nuclear test ban in 1962 showed an exponential decay of ¹⁴CO₂ 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 CO₂ would return to natural background values within 5 years. What do you think of this reasoning?
- 1.16 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 τ_1 against transfer to reservoir 2, and water in reservoir 2 (mass m_2) has a residence time τ_2 against transfer to reservoir 1. Show that the characteristic mixing time τ 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 τ larger or smaller than τ_1 and τ_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 CO₂ uptake

*Daniel J. Jacob, Supplemental Problems for
“Introduction to Atmospheric Chemistry”, 13th edition, 2021
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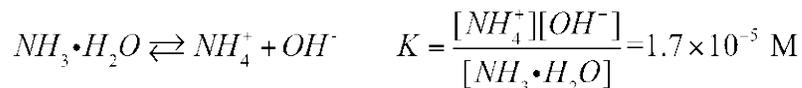
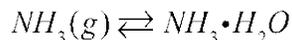
The alkalinity of the present-day ocean is 2.3×10^{-3} M. The pH is 8.2. Assume the ocean to be well mixed. Infer the CO_3^{2-} concentration in the ocean, using the equilibrium constant



Assuming that uptake of atmospheric CO_2 by the ocean conserves ocean alkalinity, show that this places an upper limit of 1600 ppmv for the total amount of additional atmospheric CO_2 that could be taken up by the ocean.

4. Ocean alkalinity and ammonia

Ocean alkalinity is generally viewed as a conserved quantity but that's not strictly true. For example, industrial fertilizer production of ammonia leads to large agricultural emissions of ammonia to the atmosphere. Ammonia is water-soluble and efficiently removed from the atmosphere by wet deposition, some going into the oceans. The relevant equilibria are



- 4.1 Explain how ammonia deposition effectively increases the alkalinity of the ocean [Hint: calculate the $[\text{NH}_4^+]/[\text{NH}_3 \cdot \text{H}_2\text{O}]$ ratio at ocean pH, and conclude whether most of deposited NH_3 is present as $\text{NH}_3 \cdot \text{H}_2\text{O}$ or as NH_4^+]. Write a stoichiometric equilibrium showing the one-to-one uptake of ammonia and CO_2 by the ocean.
- 4.2 We could imagine producing ammonia industrially and dumping it to the ocean solely for the purpose of increasing ocean alkalinity and thus CO_2 uptake by the ocean. The present-day source of CO_2 from fossil fuel combustion is 8 Pg C a^{-1} . Assuming a fixed ocean pH, show that 10 Pg N a^{-1} of industrial production would be needed to take up all of that CO_2 .
- 4.3 The marine biosphere is presently little affected by anthropogenic nitrogen on a global scale. Briefly explain why, using the box model of the nitrogen cycle in the book (Figure 6.3). Would that change if we carried out the plan described in the previous question?

5. 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 $10 \times 10 \text{ m}^2$ 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.

- 5.1 Our first concern is depletion of oxygen. Show that we will run out of oxygen in 7 days.
- 5.2 Before running out of oxygen, however, we might die from accumulation of CO₂. At a mixing ratio of 0.03, CO₂ becomes toxic. Assuming no removal of CO₂ from the room, show that this level of CO₂ is reached in about a day.
- 5.3 We can attempt to remove this CO₂ chemically by continuously bubbling the air in the room through a water solution saturated with calcium carbonate (CaCO₃). Explain briefly how this would work.
- 5.4 Would this bubbler also work to replenish O₂? Briefly explain.

6. Measuring CO₂ from space

Column concentrations of CO₂ 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 CO₂ 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⁻¹. We further assume that the air upwind contains a uniform background CO₂ mixing ratio.

- 6.1 The CO₂ surface flux in the East Asian region is estimated to peak in March at 1×10^{11} mol day⁻¹ (net emission) and to be minimum in August at -1×10^{11} mol day⁻¹ (net uptake). Show that the corresponding seasonal variation of the CO₂ mixing ratio in the region relative to the background is ± 0.2 ppm. Roughly what percentage of the CO₂ background does that represent? Measuring any gas with better than 1% precision is difficult. We see that measuring CO₂ from space is a major challenge!
- 6.2 The satellite instrument doesn't actually measure a CO₂ mixing ratio but rather a column concentration Ω_{CO_2} (molecules cm⁻²). Show that without simultaneous accurate knowledge of the local surface pressure the measurement would be useless.
- 6.3 A solution is to have the instrument measure the O₂ column concentration Ω_{O_2} together with that of CO₂, taking advantage of O₂ absorption features in the near-IR. Briefly explain how one can obtain CO₂ mixing ratio information in this manner.

7. Terrestrial sink of CO₂

We examine here the constraints offered by atmospheric CO₂ observations on the rate of carbon uptake by the terrestrial biosphere.

- 7.1 Atmospheric CO₂ concentrations increased by 1.5 ppm a⁻¹ during the decade of the 1990s. During that time the fossil fuel source was 6.3 Pg C a⁻¹ and the net uptake by the ocean was 1.7 Pg C a⁻¹. Show that this implies net uptake of carbon by the terrestrial biosphere of 1.4 Pg C a⁻¹.
- 7.2 Mean observed CO₂ concentrations in the northern hemisphere are 2.5 ppm higher than in the southern hemisphere. Assume that the fossil fuel source of CO₂ 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 0th-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].
- 7.3 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 CO₂ but instead as CO and methane, which are then oxidized to CO₂ 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 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 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 Which of the following gases could act as greenhouse gases: SO_2 , NH_3 , CO , H_2 ?
- 1.6 Radiative absorption by CO_2 is particularly efficient in the $15 \text{ }\mu\text{m}$ band yet this band makes little contribution to the greenhouse forcing from added CO_2 . Explain this apparent contradiction.
- 1.7 You wish to launch a satellite to measure sea surface temperatures. What would be a good observing wavelength to choose?
- 1.8 You wish to launch a satellite to measure atmospheric CO_2 using terrestrial radiation. What would be a good observing wavelength to choose?
- 1.9 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.
- 1.10 Stratospheric ozone has both a cooling and warming effect on the Earth's surface temperature. Why does it cause cooling? Why does it cause warming?
- 1.11 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.
- 1.12 Clouds scatter radiation at visible wavelengths but absorb radiation at infrared wavelengths. This decreases the diurnal temperature range (difference between daytime maximum and nighttime minimum temperatures). Explain why.
- 1.13 Tropical deforestation converts dark green forests to brighter surfaces, increasing the albedo of the Earth. Using the simple radiative budget model for the Earth's surface temperature constructed in class, calculate the decrease in the mean surface temperature of the Earth that would result from a 1% increase in the Earth's albedo.

- 1.14 A climate skeptic argues, “It’s ridiculous to think that CO₂ could be causing climate warming, considering that water vapor is so much more important than CO₂ as a greenhouse gas!” How do you respond?

2. Observing wildfires from space

The MODIS satellite instrument detects wildfires from space by measuring radiation emitted by the Earth at 4.0 μm . 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 μm .
- 2.2 It would seem logical then to detect wildfires by observing radiation at 3.2 μm , but in fact 4.0 μm is much better. Explain why. [*Hint: see Fig. 7-11 of book*]
- 2.3 At 4.0 μm , 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 CO₂ could be countered by injections of SO₂ in the stratosphere to produce sulfate aerosol.

- 3.1 It is estimated that injecting one ton of sulfur as SO₂ 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 ΔF for that 1-year period would be $1.4 \times 10^{-5} \text{ W m}^{-2}$.
- 3.3 We would like to use these SO₂ injections to maintain the climate at its present state, canceling the effect of future growth of CO₂. The present-day CO₂ concentration is 380 ppm with a growth rate of 1.5 ppm a^{-1} . The radiative forcing ΔF (W m^{-2}) from increasing the CO₂ mixing ratio from C_0 to C can be approximated as $\Delta F = 6.3 \ln(C/C_0)$. 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 CO₂ 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. Cooling of the stratosphere by greenhouse gases

Consider the stratosphere as a single isothermal layer of temperature T_S containing ozone and CO₂. Ozone in this layer absorbs a fraction f_1 of the incoming solar radiation flux F [W m^{-2}]. CO₂ in this layer absorbs a fraction f_2 of the terrestrial radiation upwelling from the troposphere. We describe this upwelling terrestrial

radiation with a blackbody radiative flux σT_T^4 , where T_T is an effective temperature for the troposphere.

- 4.1 From equilibrium between absorbed and emitted radiation for this stratospheric layer, show that

$$T_s = \left(\frac{f_1 F + f_2 \sigma T_T^4}{2f_2 \sigma} \right)^{1/4}$$

- 4.2 Show from this equation that T_s decreases as f_2 increases [Hint: show that the derivative dT_s^4/df_2 is negative]. Conclude as to the effect of increasing CO₂ on stratospheric temperatures.

5. 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.

- 5.1 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 σ is the Stefan-Boltzmann constant.
- 5.2 Show that $df = \gamma C n_a(0) \exp[-z/H] dz$ where γ 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 σ as notation for the absorption cross-section but we use γ here to avoid confusion with the Stefan-Boltzmann constant]
- 5.3 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 $x \ll 1$].
- 5.4 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 $z \rightarrow \infty$.

- 5.5 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?

6. 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.

- 6.1 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%.
- 6.2 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?
- 6.3 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%.
- 6.4 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 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 W m^{-2} .
- 6.5 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.

7. 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.

- 7.1 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 .
- 7.2 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 α 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?
- 7.3 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.
- 7.4 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 CO₂ emissions. Briefly explain.
- 7.5 It has thus been argued that controlling methane emissions could “buy us time” by allowing to delay CO₂ 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 ΔT affects the emission of terrestrial radiation to space]

8. Vertical dependence of the radiative forcing efficiency of black carbon

Black carbon (BC) particles emitted by combustion absorb solar radiation and are transparent to IR radiation. We show here that the BC radiative forcing depends strongly on whether the BC particles are above or below clouds. Assume for this problem that the only contributors to the Earth’s planetary albedo of 0.28 are clouds and the Earth’s surface, and that there are no multiple reflections (that is, solar radiation can only be reflected once).

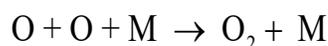
- 8.1 We first need an estimate of the mean cloud albedo. Assume for this purpose that 70% of the Earth's area is covered by clouds, that this cloud fraction is evenly distributed over the Earth, and that the albedo of the Earth surface is 0.05. Show that the mean cloud albedo is 0.35.
- 8.2 Let us model the clouds as a thin sheet at 5 km altitude separating the lower troposphere from the upper troposphere over 70% of the Earth, and the BC layer as another thin sheet covering the entire Earth and absorbing a fraction of all solar radiation that traverses it. Show that the radiative forcing from this BC layer is 8 times larger if it is in the upper troposphere than if it is in the lower troposphere.
- 8.3 Lifting of BC particles from the lower to the upper troposphere is however limited by precipitation scavenging. We can estimate this scavenging efficiency by assuming similarity between BC and water vapor. Consider an air parcel at the surface with a surface temperature of 288 K and 50% relative humidity. As this air parcel is lifted to 5 km, what fraction of the initial water vapor is lost to precipitation? Assume a mean adiabatic lapse rate of 6.5 K km^{-1} and a scale height of 7.4 km.

CHAPTER 10: STRATOSPHERIC CHEMISTRY

1. Short questions

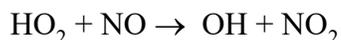
- 1.1 Consider harmful UV radiation for which the ozone layer has an optical depth of 10. The ozone layer has thinned by 4% since 1970, with a corresponding 4% decrease in optical depth. What is the resulting percent increase in the flux of this UV radiation at the surface of the Earth?

- 1.2 The original Chapman mechanism included a fifth reaction:



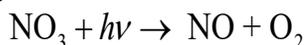
What is the effect of this reaction on ozone? Is it more important in the lower or in the upper stratosphere? Briefly explain. *[We don't include this reaction in the standard description of the Chapman mechanism because it is of negligible importance]*

- 1.3 Would you expect O and O₃ concentrations in the stratosphere to vary with time of day, and if so how?
- 1.4 The sensitivity of ozone to the atmospheric O₂ concentration is strongly buffered, meaning that a change in O₂ results in a much smaller change in O₃. Why?
- 1.5 Oxidation of NO to NO₂ can take place by



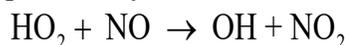
Assuming that NO₂ goes on to photolyze and that OH goes on to react with ozone, what is the net effect of this reaction on stratospheric ozone? *[Hint: build a closed propagation cycle starting from this reaction and determine the net effect of the cycle on ozone].*

- 1.6 A minor branch of NO₃ photolysis is



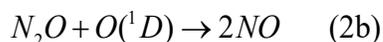
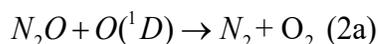
How does this reaction affect ozone?

- 1.7 Oxidation of NO to NO₂ can proceed by



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

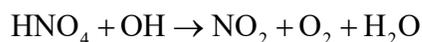
- 1.8 N₂O in the stratosphere can either photolyze or be oxidized by O(¹D):



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

- 1.9 It has been argued that a fleet of supersonic aircraft releasing NO_x in the lower stratosphere could actually be beneficial to ozone by decreasing the rate of chlorine-catalyzed ozone loss. How would that work?

- 1.10 Peroxynitric acid (HNO_4) is produced and removed in the stratosphere by



What is the effect on stratospheric ozone? Think of the effects on both NO_x and HO_x .

- 1.11 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 $\text{O}_3 + \text{O}$ reaction accounts for only 10% of the O_x sink. Can you reconcile these two results?
- 1.12 The stability of hydrogen halides decreases as $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$. What does that mean for the efficiency of different halogens in destroying ozone?
- 1.13 If temperatures in the wintertime Antarctic stratosphere were not so cold, the ClO dimer would thermally decompose by $\text{ClOOC} + \text{M} \rightarrow \text{ClO} + \text{ClO} + \text{M}$ rather than photolyze. What would be the effect of this thermolysis on Antarctic ozone depletion?
- 1.14 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 higher further south, where temperatures are lower and allow more PSCs to form?
- 1.15 In the ozone hole, once ozone has been totally destroyed, the chlorine radicals are converted to HCl. Why? (Hint: think of the Cl/ClO partitioning)
- 1.16 There is concern that increasing water vapor in the stratosphere (due to rising methane) will lead to increased PSC formation. Explain why using the $\text{HNO}_3\text{-H}_2\text{O}$ phase diagram.
- 1.17 There is concern that a climate-driven increase in the frequency of very deep thunderstorms at northern mid-latitudes could result in large stratospheric ozone depletion. Explain why.

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) ($T = 273 \text{ K}$, $P = 1 \text{ atm}$) and measured the attenuation of light as it passed through the tube. They reported their result in terms of an “absorption constant” α ,

$$I = I_0 10^{-\alpha d}$$

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 α is in units of cm^{-1} and λ 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 θ as follows:

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

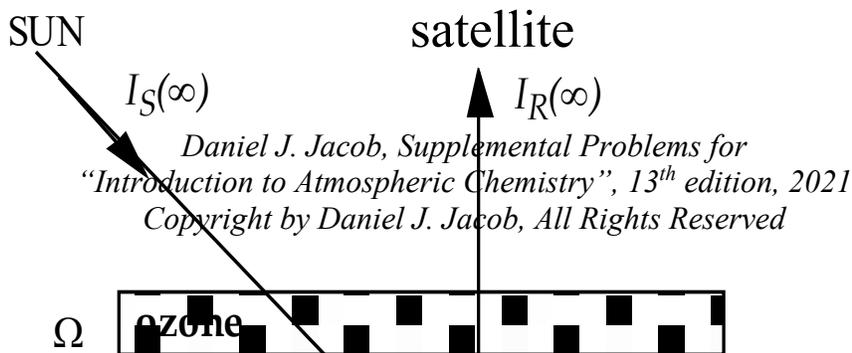
where A is a constant and λ_{\min} is in units of nm. Let I_o represent the solar radiation at the top of the atmosphere, I represent the direct solar radiation at the ground, and λ_{\min} represent the wavelength at which $I/I_o = 1/n$ where n is some constant. Show that the observations of Cornu are 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 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 Ω (molecules cm^{-2}) observed by the satellite directly overhead, with the downwelling solar radiation making an angle θ 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 λ , A the surface albedo (assumed identical at 340 and 380 nm), and σ 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 $1\% \text{ a}^{-1}$ during the 1990s, for reasons that are unclear. Methane itself increased in the atmosphere at a rate of $1\% \text{ a}^{-1}$ 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 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

*Daniel J. Jacob, Supplemental Problems for
 "Introduction to Atmospheric Chemistry", 13th edition, 2021
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transport of water vapor from the troposphere to the stratosphere must have been more important.]

5. HO_x-catalyzed ozone loss in the stratosphere

Consider the following HO_x-catalyzed chain mechanism for destruction of stratospheric ozone:

1. $O_3 + h\nu \rightarrow O_2 + O(^1D)$
2. $O(^1D) + M \xrightarrow{\alpha_2} O_3 + M$
3. $O(^1D) + H_2O \rightarrow 2OH$
4. $OH + O_3 \rightarrow HO_2 + O_2$
5. $HO_2 + O_3 \rightarrow OH + 2O_2$
6. $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$
7. $H_2O_2 + h\nu \rightarrow 2OH$
8. $OH + HO_2 \rightarrow H_2O + O_2$

Let k_i denote the rate constant of reaction i . Make the following assumptions:

- Rate (2) \gg Rate (3);
- The chain propagation steps are much faster than the initiation and termination steps;
- $O(^1D)$, OH, HO₂, and H₂O₂ are in steady state.

- 5.1 Draw a diagram of the mechanism illustrating the conversion between the species H₂O, OH, HO₂, and H₂O₂. Identify which of these species are radicals and which is a reservoir. Identify the initiation, propagation, and termination steps in the chain.
- 5.2 Show that $[O(^1D)] = k_1[O_3]/k_2[M]$.
- 5.3 Show that $[OH]/[HO_2] = k_5/k_4$.
- 5.4 It is useful to define the chemical family HO_y \equiv OH + HO₂ + 2H₂O₂. Explain what this family represents and why H₂O₂ should be counted as two HO_y's. Write a steady-state equation for that family (you will use it in the next question).
- 5.5 Using results from the previous questions, show that the HO_x-catalyzed ozone loss rate in the above mechanism is given by

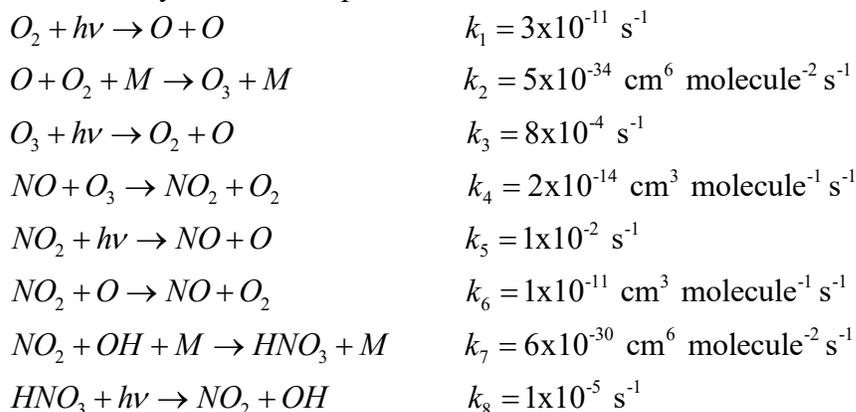
$$\frac{-d[O_3]}{dt} = 2 \left(\frac{k_1 k_3 k_4 k_5}{k_2 k_8 [M]} \right)^{1/2} [H_2O]^{1/2} [O_3]^{3/2}$$

- 5.6 A remarkable feature of this ozone loss rate expression is its non-linear dependences on [H₂O] and [O₃]. Explain how this moderates the sensitivity of ozone to changes in H₂O and O₃ (as compared to linear dependences).
- 5.7 Another remarkable feature of this ozone loss rate expression is that it is insensitive to the formation of the H₂O₂ reservoir. For the NO_x- and ClO_x-catalyzed ozone loss cycles, we saw that formation of the reservoirs (HNO₃, HCl, ClNO₃) slowed down the ozone loss rate; but this is not the case for H₂O₂ here. Explain the difference.

[Hint: there is a major difference between the sink of HO_y and the sinks of NO_y and Cl_y]

6. NO_x-catalyzed ozone loss in the stratosphere

Consider an air parcel at 30 km altitude under mid-latitude equinox noontime conditions with $T = 230$ K, $[O_3] = 2 \times 10^{12}$ molecules cm⁻³, $[OH] = 1 \times 10^7$ molecules cm⁻³, $[NO] = 1 \times 10^9$ molecules cm⁻³. Assume the following simplified mechanism to describe NO_x-catalyzed ozone depletion:



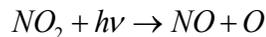
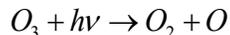
Rates for reactions (2) and (7) are at the low-pressure limit.

- 6.1 Calculate the steady-state concentrations of O and NO₂ [Hint: make your life easier by considering only the most important reactions]. You should find $[O] = 5 \times 10^7$ molecules cm⁻³, $[NO_2] = 4 \times 10^9$ molecules cm⁻³.
- 6.2 Calculate the rate of ozone loss by the NO_x-catalyzed cycle in this air parcel. Compare to the rate of O_x formation in the air parcel. What do you conclude?
- 6.3 Calculate the NO_x/HNO₃ concentration ratio, assuming steady-state for HNO₃. Comment on the importance of HNO₃ as a NO_x reservoir. If HNO₃ formation did not take place, how much faster would NO_x-catalyzed ozone loss be?

7. Expanding the definition of the odd oxygen family

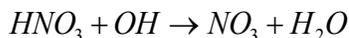
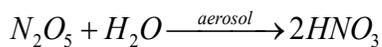
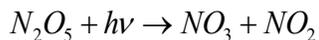
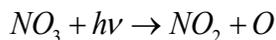
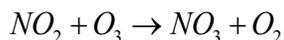
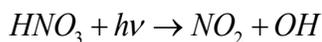
Accounting for the sources and sinks of ozone in the stratosphere can be made easier by expanding the odd oxygen (O_x) family from its original O_x ≡ O₃ + O definition. The directing idea is that since O_x is produced from O₂, then the loss of O_x should involve reconversion to O₂. We consider here the application of this idea to nitrogen oxides.

- 7.1 Consider first the cycling between O₃, O, and NO₂ by the dominant null cycles:



Explain why it would make sense to include NO_2 as part of the O_x family so that $[O_x] = [O_3] + [O] + [NO_2]$.

- 7.2 We showed in class that the rate of NO_x -catalyzed ozone loss is given by twice the rate of the $NO_2 + O$ reaction. Show that this result can be immediately derived by considering NO_2 as part of the O_x family.
- 7.3 One can further expand the O_x family by including NO_3 , N_2O_5 , and HNO_3 as members. Consider the following mechanism cycling NO_y species in the stratosphere:



By considering the null cycles in this mechanism, show that the definition of the O_x family can be expanded usefully as follows:

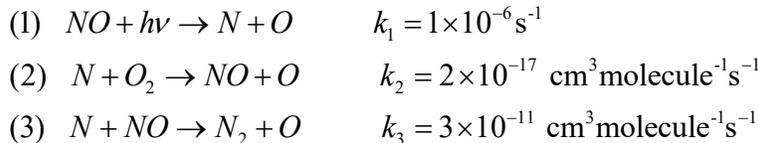
$$[O_x] = [O_3] + [O] + [NO_2] + [HNO_3] + 2[NO_3] + 3[N_2O_5]$$

Explain the multiplicative coefficients for NO_3 and N_2O_5 .

- 7.4 Using this expanded definition of the O_x family, identify a cycle involving HNO_3 formation and loss that represents a source of O_3 and one that represents a sink of O_3 .

8. Chemical loss of NO_y in the upper stratosphere

The reactive nitrogen oxides family (NO_y) responsible for catalytic loss of stratospheric ozone is removed from the stratosphere by transport to the troposphere (once in the troposphere, NO_y is efficiently scavenged by precipitation). An additional sink for stratospheric NO_y 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_y budget.

- 8.1 For a typical NO_y concentration of 15 ppb at 40 km altitude, show that Rate (2) \gg Rate (3).
- 8.2 Assuming that N atoms are in steady state and that Rate (2) \gg Rate (3), show that the NO_y chemical loss rate $L(\text{NO}_y)$ ($\text{molecules cm}^{-3} \text{ s}^{-1}$) is given by

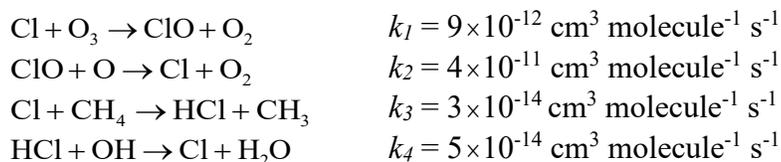
$$L(\text{NO}_y) = \frac{2k_1 k_3 f^2}{k_2 [\text{O}_2]} [\text{NO}_y]^2$$

where f is the fraction of NO_y present as NO.

- 8.3 Calculate the resulting lifetime of NO_y 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_y lifetime of 0.6 years.
- 8.4 Assuming that this chemical sink operates only in the upper stratosphere above 10 hPa, and that NO_y is well mixed in the stratosphere, comment qualitatively on its importance relative to the loss of stratospheric NO_y by transfer to the troposphere.

9. 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) $[\text{O}_3] = 3 \times 10^{12} \text{ molecules cm}^{-3}$, $[\text{O}] = 2 \times 10^7 \text{ molecules cm}^{-3}$, $[\text{CH}_4] = 7 \times 10^{11} \text{ molecules cm}^{-3}$, $[\text{OH}] = 2 \times 10^6 \text{ molecules cm}^{-3}$.

- 9.1 Assuming steady state for all Cl_y species, calculate the fractional contribution of each species to total Cl_y .
- 9.2 We define the *ozone depletion efficiency* of chlorine as the total number of ozone molecules destroyed by a molecule of Cl_y in the stratosphere before this Cl_y is ultimately transported to the troposphere and removed by deposition. Calculate the ozone depletion efficiency of chlorine by making the following assumptions:

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 "Introduction to Atmospheric Chemistry", 13th edition, 2021
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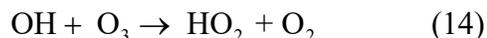
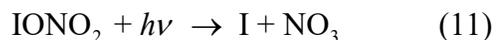
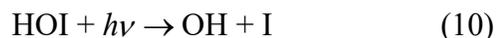
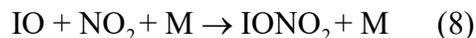
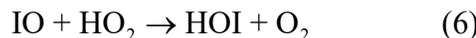
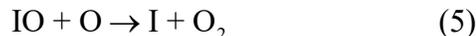
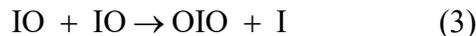
- The conditions given at the beginning of the problem apply to the whole stratosphere;
 - The lifetime of air in the stratosphere is 2 years;
 - Chlorine transported to the troposphere is removed by deposition.
- 9.3 Other halogen atoms ($X \equiv \text{F, Br, I}$) destroy ozone by catalytic mechanisms 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.
- 9.4 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 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 CFC1_3 (CFC-11):

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

Consider 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: $\text{H} = 1 \text{ g mol}^{-1}$, $\text{C} = 12 \text{ g mol}^{-1}$, $\text{Cl} = 35.5 \text{ g mol}^{-1}$, $\text{F} = 19 \text{ g mol}^{-1}$].

10. Iodine chemistry

Iodine radicals are produced in the stratosphere by photolysis of methyl iodide (CH_3I) emitted by the oceans. Consider the following mechanism for iodine chemistry:

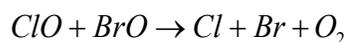
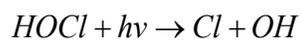
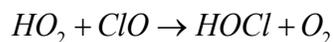
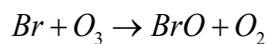
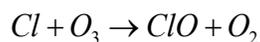
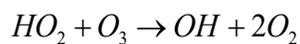
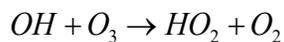


- 10.1 Draw a diagram of the iodine cycle by the above mechanism. Identify which iodine species are radicals.
- 10.2 Identify three catalytic cycles for ozone loss.
- 10.3 Determine the rate-limiting step for each of the catalytic cycles for ozone loss, and write an overall equation for the ozone loss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

11. Convective injection of water vapor into the mid-latitudes stratosphere

Recent aircraft observations over the central US have revealed large thunderstorm injections of water vapor into the lower stratosphere.

- 11.1 Global warming is expected to result in deeper thunderstorms, and there is concern that the resulting injection of water vapor into the lower stratosphere could represent a positive feedback to the warming. Explain briefly why.
- 11.2 There is also concern that this injection of water vapor into the lower stratosphere could drive ozone depletion. Major radical propagation reactions in the mid-latitudes lower stratosphere include:



Identify in the above mechanism three different catalytic cycles for ozone loss.

Two of these would be accelerated by increasing water vapor; identify which ones and explain briefly why.

- 11.3 There is further concern that an increase of water vapor in the mid-latitudes lower stratosphere could drive PSC formation even though temperatures are not as cold as in the Antarctic stratosphere. From the H₂O-HNO₃ phase diagram in Figure 10.12 of the textbook, explain why an increase of water vapor would allow formation of PSCs at warmer temperature. Which of the above three catalytic cycles for ozone loss would be accelerated by PSC formation?

CHAPTER 11: GLOBAL TROPOSPHERIC CHEMISTRY

1. Short questions

- 1.1 Will stratospheric ozone recovery over the coming decades cause an increase or a decrease of tropospheric OH?
- 1.2 HO_x radicals 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_nH_{2n+2} 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_x source to the atmosphere were to double, would the NO_x 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? [Hint: think about the effect of increasing methane on OH]
- 1.7 We saw in chapter 7 that the radiative forcing from increase in methane concentrations since preindustrial times is 0.45 W m⁻². However, the radiative forcing from increase in methane emissions since pre-industrial times is much larger than that because atmospheric oxidation of methane produces additional greenhouse gases. Explain.
- 1.8 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. Why is that?
- 1.9 When NO_x concentrations are sufficiently high, PAN formation does not depend on NO_x but instead increases with increasing ozone. Why?
- 1.10 Tropospheric ozone concentrations outside of polluted regions generally increase with altitude. Why would that be?
- 1.11 NO reacts with ozone in the troposphere, like it does in the stratosphere. Show that this reaction drives a null cycle for ozone but also acts to decrease ozone production as the ozone concentration increases. [Hint: think of the effect on the [NO]/NO₂ ratio].
- 1.12 Anthropogenic methane emission is thought to an important driver for global increase in tropospheric ozone, even though ozone production is globally NO_x-limited. Why?

2. Explosive vs. dissipative behavior

A remarkable property of atmospheric chemical systems is that they do not lead to explosive behavior, except in contrived situations. To understand explosive behavior, consider a simple system where X is oxidized catalytically by OH to produce Y, which photolyzes to produce OH (this is not too dissimilar to the oxidation of methane, producing formaldehyde which photolyzes). OH can also be scavenged by aerosols. So we have three reactions:

1. $X + OH \longrightarrow Y + OH$
2. $Y + h\nu \longrightarrow OH + \text{products}$
3. $OH \xrightarrow{\text{aerosol}} \text{products}$

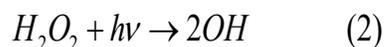
where “products” are assumed inert. Assuming steady state for Y, show from the kinetic equations that this mechanism will either consume X explosively or will shut itself down, depending on the initial concentration of X.

3. HO_x radical loss catalyzed by Cu/Fe cycling in aqueous aerosols

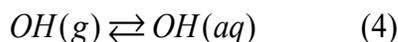
The dominant gas-phase sink for HO_x radicals in the troposphere is



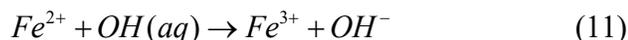
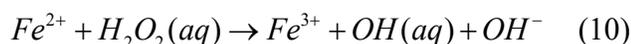
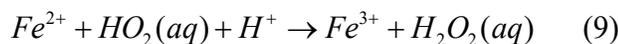
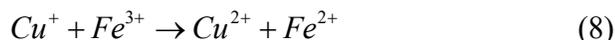
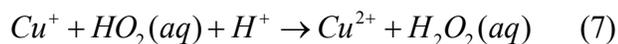
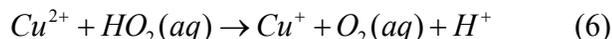
However, this is not a terminal sink because H₂O₂ can be photolyzed back to HO_x radicals:



Atmospheric observations suggest that loss of HO_x 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 HO₂ in aqueous aerosols and subsequent reactions involving redox cycling of copper and iron ions. Consider the three Henry’s law equilibria by which HO₂, OH, and H₂O₂ 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:



- 3.1 Write four different catalytic Cu and Fe catalytic cycles starting from reaction (6) and briefly explain how each of these would contribute to HO_x loss.
- 3.2 Does the presence of Fe in the aerosol increase HO_x loss relative to the presence of Cu alone?

4. Radiative forcing of NO_x and methane

- 4.1 Explain three ways in which NO_x emissions can affect climate, and the sign of the associated radiative forcing for each.
- 4.2 The radiative forcing from anthropogenic methane in the present-day vs. pre-industrial atmosphere is 0.5 W m⁻² when referenced to the increase in methane *concentration* but 0.85 W m⁻² when referenced to methane anthropogenic *emission*. Explain the difference.
- 4.3 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_x and methane. Explain briefly why methane is important in determining the global ozone concentration even though the ozone production rate is NO_x-limited.
- 4.4 A strategy to reduce global tropospheric ozone from both a pollution and climate perspective must focus on reducing methane emissions rather than NO_x. However, a strategy to reduce ozone smog locally must focus on reducing NO_x emissions rather than methane. Explain these two apparently contradictory statements.

5. Ozone increase with altitude in the background troposphere

Ozone increases with altitude in the background troposphere and here we examine why. Consider the following simplified chemical mechanism for production and loss of tropospheric ozone:

- 1.
- (R1) $O_3 + h\nu \longrightarrow O_2 + O(^1D)$
 (R2) $O(^1D) + M \xrightarrow{O_2} O_3 + M$
 (R3) $O(^1D) + H_2O \longrightarrow 2OH$
 (R4) $CO + OH \xrightarrow{O_2} CO_2 + HO_2$
 (R5) $HO_2 + NO \longrightarrow OH + NO_2$
 (R6) $O_3 + NO \longrightarrow O_2 + NO_2$
 (R7) $NO_2 + h\nu \xrightarrow{O_2} NO + O_3$
 (R8) $HO_2 + HO_2 \longrightarrow H_2O_2 + O_2$

Let R_i represent the rate of reaction (Ri) and k_i the corresponding rate constant. Assume throughout this problem that $R_3 \ll R_2$, $R_5 \ll R_6$, and $[NO] \ll [NO_2]$.

- 5.1 Which reaction in the mechanism is a source of HO_x radicals ($HO_x \equiv OH + HO_2$)? Which reaction is a sink of HO_x ?
- 5.2 Show that the HO_x production rate P_{HO_x} is given by

$$P_{HO_x} = \frac{2k_1k_3 [O_3][H_2O]}{k_2 [M]}$$

[Hint: assume steady state for $O(^1D)$]

- 5.3 From steady-state for the HO_x radicals, show that

$$[HO_2] = \left(\frac{k_1k_3 [O_3][H_2O]}{k_2k_8 [M]} \right)^{1/2}$$

- 5.4 From steady-state for the NO_x radicals, show that

$$[NO] = \frac{k_7[NO_x]}{k_6[O_3]}$$

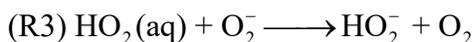
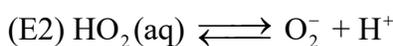
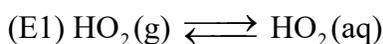
- 5.5 Reaction (R5) is the rate-limiting step for ozone production, and reaction (R3) is the rate-limiting step for ozone loss. Briefly explain why.
- 5.6 Assuming steady-state for ozone between production by (R5) and loss by (R3), show that

$$[\text{O}_3] = \left(\frac{k_5 k_7 [\text{NO}_x]}{k_6} \right)^{2/3} \left(\frac{k_2}{k_1 k_3 k_8 C_{\text{H}_2\text{O}}} \right)^{1/3}$$

where $C_{\text{H}_2\text{O}}$ is the water vapor mixing ratio. From this equation, explain how the vertical trend of water vapor drives an increase of ozone with altitude in the troposphere.

6. HO₂ uptake by clouds

Reactive uptake of gas-phase HO₂ by cloud droplets follows well-established aqueous-phase chemistry:



Let K_i represent the equilibrium constant for equilibrium (Ei) and k represent the rate constant for aqueous-phase reaction (R3).

- 6.1 Write a net reaction for this mechanism, and show that it is stoichiometrically equivalent to a common gas-phase HO_x radical loss pathway.
- 6.2 Show that the HO₂ loss rate from this mechanism is given by

$$-\frac{d\{\text{HO}_2\}}{dt} = \frac{2LkK_2K_1^2 p_{\text{HO}_2}^2}{[\text{H}^+]}$$

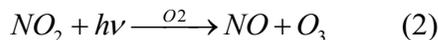
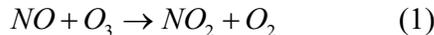
where L is the liquid water content of the cloud (liters of water per liter of air), and $\{\text{HO}_2\}$ is the HO₂ concentration in units of moles per liter of air.

- 6.3 For typical cloudy conditions we find that HO₂ has a lifetime of 1 minute against this mechanism, as compared to a lifetime of 3 minutes against reaction with NO. Conclude as to the importance of this mechanism for suppression of ozone formation under cloudy conditions.

7. Ozone production from lightning

Lightning NO_x is a very efficient source of tropospheric ozone because it is emitted in the upper troposphere where the lifetime of NO_x is long. Assume that the loss of NO_x is by conversion of NO₂ to HNO₃.

- 7.1 Show that the lifetime of NO_x is proportional to $(1 + \frac{[\text{NO}]}{[\text{NO}_2]})$
- 7.2 The NO/NO_2 concentration ratio is largely controlled by the null cycle



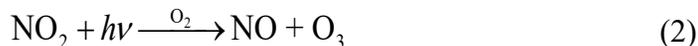
Derive from this mechanism an expression for the NO/NO_2 concentration ratio as a function of k_1 , k_2 , and $[\text{O}_3]$. Calculate the value of this ratio in the upper troposphere (10 km altitude, $T = 220$ K, 80 ppb O_3) and in surface air (0 km, $T = 300$ K, 30 ppb O_3) using $k_1 = 2 \times 10^{-12} \exp[-1400/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $k_2 = 1 \times 10^{-2} \text{ s}^{-1}$, and a scale height $H = 7.4$ km. You should find that the NO/NO_2 concentration ratio is much larger in the upper troposphere than in surface air, implying a much longer lifetime for NO_x .

8. Mapping NO_x emissions using satellites

Nitrogen dioxide (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 NO_x .

- 8.1 We first examine the relative contributions of the troposphere and the stratosphere to the total mass of NO_x in the atmosphere. The global emission of NO_x to the troposphere, E_{NO_x} , is about 50 Tg N a^{-1} . Assuming a lifetime $\tau_{\text{NO}_x} = 1$ day against oxidation to HNO_3 , and further assuming that HNO_3 is removed solely by deposition, calculate the mass of NO_x in the troposphere in unit of Tg N.
- 8.2 The global mean mixing ratio of N_2O is 310 ppb and the atmospheric lifetime of N_2O is 114 years. All of the N_2O loss is in the stratosphere. Assuming that 5% of N_2O loss produces NO_x , that the NO_x/NO_y molar ratio in the stratosphere is 0.1, and that the lifetime of NO_y in the stratosphere is 1 year, estimate the mass of NO_x in the stratosphere in unit of Tg N. You should find that this mass is less than that in the troposphere but is not negligible.
- 8.3 We can remove the contribution of the stratosphere in various ways. After this subtraction we are left with a measurement of the tropospheric column Ω of NO_2 . Express Ω as a function of local values of E_{NO_x} , τ_{NO_x} , and $[\text{NO}_2]/[\text{NO}_x]$, assuming local steady state for NO_x and further assuming that τ_{NO_x} and $[\text{NO}_2]/[\text{NO}_x]$ are uniform in the column.
- 8.4 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 NO and NO_2 :

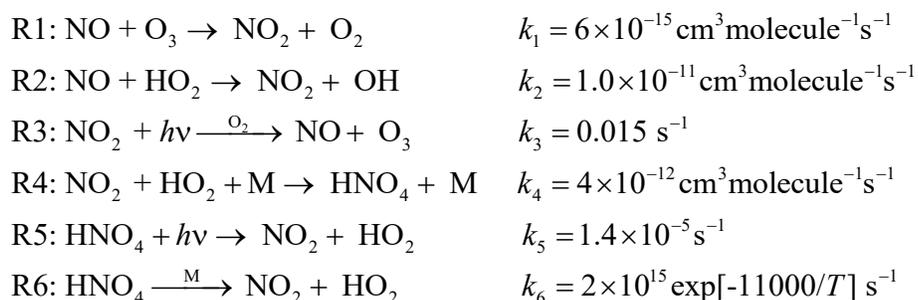




with rate constants $k_1 = 2 \times 10^{-12} \exp[-1400/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k_2 = 1 \times 10^{-2} \text{ s}^{-1}$. Assuming a uniform O_3 mixing ratio of 50 ppb, calculate the $[\text{NO}_2]/[\text{NO}_x]$ ratio at sea level ($T = 290 \text{ K}$) and at 10 km altitude ($T = 220 \text{ K}$). On the basis of this result, would you expect the satellite to more easily detect emissions of NO_x at the surface, or in the upper troposphere (such as from lightning?)

9. NO_x partitioning in the upper troposphere

Consider the following mechanism cycling NO_x and HNO_4 in the upper troposphere:



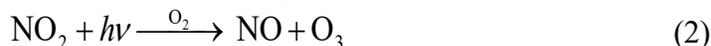
Assume typical conditions for the upper troposphere of $[\text{O}_3] = 6 \times 10^{11} \text{ molecules cm}^{-3}$, $[\text{HO}_2] = 8 \times 10^7 \text{ molecules cm}^{-3}$, and $T = 240 \text{ K}$. Assume R4 to be in the high-pressure limit so that the rate constant k_4 is independent of $[\text{M}]$ as reflected by its units.

- 9.1 Draw a diagram showing the cycling between nitrogen species. Identify radical and reservoir nitrogen species. Identify a catalytic cycle for ozone production.
- 9.2 Calculate the $[\text{NO}]/[\text{NO}_2]$ concentration ratio at steady state. Show that you can neglect the cycling with HNO_4 in this calculation [*Hint: show that rate (R4) \ll rate (R3)*]. You should find $[\text{NO}]/[\text{NO}_2] = 3.4 \text{ mol mol}^{-1}$.
- 9.3 Calculate the $[\text{HNO}_4]/[\text{NO}_x]$ concentration ratio. You should find a value of 1.9. This makes HNO_4 an important reservoir for NO_x in the upper troposphere. By contrast, HNO_4 is not an important reservoir for NO_x in surface air ($T = 300 \text{ K}$). Explain why.
- 9.4 Measurements of the $[\text{NO}]/[\text{NO}_2]$ concentration ratio in the upper troposphere show a value of 1.7 mol mol^{-1} , or half of the value calculated above. It has been argued that this could be caused by decomposition of HNO_4 at the high temperatures of the instrument inlet. Explain how this would affect the observed $[\text{NO}]/[\text{NO}_2]$ concentration ratio.
- 9.5 Another possible explanation for the overestimate of the $[\text{NO}]/[\text{NO}_2]$ ratio is uncertainty in the rate constants k_1 , k_2 , and k_3 . The uncertainties for each rate constant are estimated to be at most 40% under upper tropospheric conditions. Could uncertainties in the rate constants reconcile the calculated and observed

- [NO]/[NO₂] ratio? Explain which two rate constants matter in this reconciliation and what adjustments could account for the observed [NO]/[NO₂] ratio.
- 9.6 If the actual [NO]/[NO₂] ratio is indeed lower than computed from models, does this make the actual ozone production more likely to be NO_x-limited, or more likely to be NO_x-saturated? Explain.

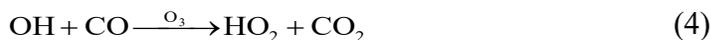
10. Chemical regimes in the upper troposphere

Aircraft emissions of 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 NO_x in the upper troposphere under different conditions. The NO_x radicals (NO_x ≡ NO + NO₂) cycle through the reactions:



Assume that the [NO]/[NO₂] ratio is determined solely by reactions (1)-(2) (a reasonable approximation in the upper troposphere). For the rest of this problem, write [NO] = α[NO_x] and [NO₂] = (1-α)[NO_x] where α is a coefficient assumed constant.

The HO_x radicals (HO_x ≡ OH + HO₂) 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:

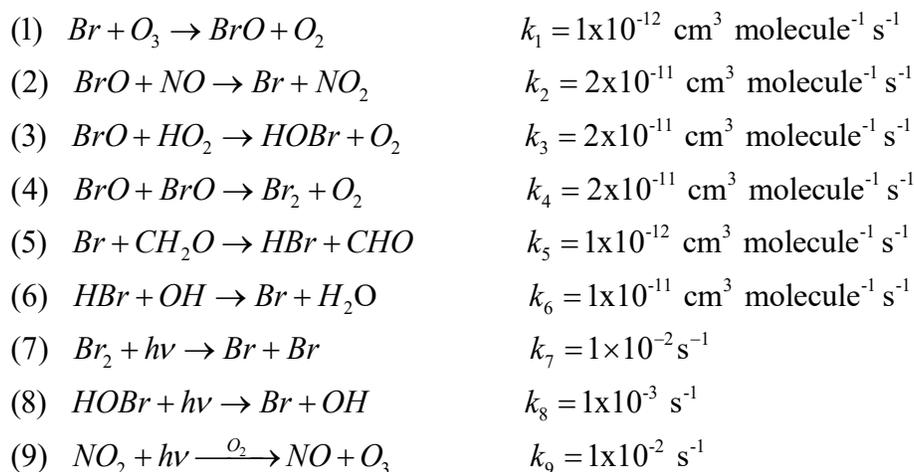


- 10.1 Identify four different HO_x sinks in the above mechanism.
- 10.2 We can distinguish four different chemical regimes in the upper troposphere depending on the dominant reaction for HO_x loss. Let us model each of these regimes by considering the limiting case where loss of HO_x is exclusively by the dominant reaction. Further assume that the HO_x radicals are in chemical steady state, and that HO_x cycling is efficient so that the HO_x cycling reactions are much faster than the HO_x loss reactions. For each regime, determine the dependence of the ozone production rate on [NO_x].

- 10.3 Which of the four regimes applies to very low NO_x concentrations? to very high NO_x concentrations? Plot qualitatively the O₃ production rate as a function of [NO_x], identifying each chemical regime in the plot. Briefly conclude as to the challenge of predicting the response of O₃ to increasing aircraft NO_x emissions.

11. Tropospheric bromine

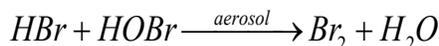
Satellite observations indicate a mean BrO concentration of 1 ppt in the troposphere. BrO at this level could represent an important tropospheric ozone sink. The dominant source of BrO in the troposphere is thought to be the photolysis and oxidation of bromoform (CHBr₃) emitted naturally by the ocean 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_y (Br_y ≡ Br + BrO + HBr + HOBr + 2Br₂):



Assume the following concentrations: [O₃] = 1 × 10¹² molecules cm⁻³, [NO] = 1 × 10⁹ molecules cm⁻³, [HO₂] = 1 × 10⁸ molecules cm⁻³, [OH] = 1 × 10⁶ molecules cm⁻³, [CH₂O] = 2 × 10⁹ molecules cm⁻³, and air density $n_a = 1 \times 10^{19}$ molecules cm⁻³. 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.

- 11.1 The mean concentration of CHBr₃ observed in the troposphere is 0.7 ppt. CHBr₃ has an atmospheric lifetime of 10 days against chemical loss, releasing three Br atoms that go on to cycle with other Br_y species by the above mechanism. Br_y 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_y is 2.1 ppt.
- 11.2 Draw a diagram of the Br_y chemical mechanism described above. Identify radical and non-radical Br_y 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.

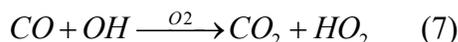
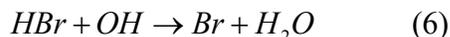
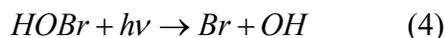
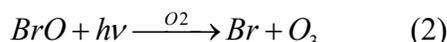
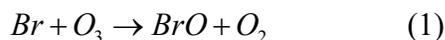
- 11.3 Let $\text{BrO}_x \equiv \text{Br} + \text{BrO}$ represent the bromine radical family. From steady state between reactions (1) and (2) show that $[\text{Br}]/[\text{BrO}] = 0.02$.
- 11.4 Calculate the resulting BrO concentration assuming that all Br_y species are in steady state. [HINT: use steady-state equations to calculate the $[\text{HBr}]/[\text{BrO}_x]$ and $[\text{HOBr}]/[\text{BrO}_x]$ ratios, making use of $[\text{BrO}] \approx [\text{BrO}_x]$ and $[\text{Br}] \approx 0.02 [\text{BrO}_x]$. For Br_2 , simply show that $[\text{Br}_2] \ll [\text{BrO}_x]$ so that Br_2 is a negligible component of Br_y . You should find $[\text{BrO}] = 0.3$ ppt.
- 11.5 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.

12. Bromine chemistry in the present and pre-industrial troposphere

Consider the following mechanism for bromine chemistry in the troposphere:



- 12.1 Draw a diagram of the cycling between bromine species by this mechanism; identify which species are radicals.
- 12.2 Identify in this mechanism a catalytic cycle for ozone loss and the corresponding rate-limiting step for ozone loss. [Hint: assume that $\text{rate}(7) \gg \text{rate}(6)$]
- 12.3 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_2O]

13. Tropospheric bromine

Recent research suggests that tropospheric bromine is a major sink for tropospheric ozone. Consider the following mechanism for tropospheric bromine:

1. $HBr + OH \rightarrow Br + H_2O$
2. $Br + O_3 \rightarrow BrO + O_2$
3. $BrO + BrO \rightarrow Br_2 + O_2$
4. $Br_2 + h\nu \rightarrow 2Br$
5. $BrO + HO_2 \rightarrow HOBr + O_2$
6. $HOBr + h\nu \rightarrow Br + OH$
7. $BrO + NO_2 + M \rightarrow BrNO_3 + M$
8. $BrNO_3 + H_2O \rightarrow HOBr + HNO_3$
9. $Br + CH_4 \rightarrow HBr + CH_3$
10. $CO + OH \xrightarrow{O_2} CO_2 + HO_2$

- 13.1 Draw a diagram showing the cycling between bromine species by this mechanism. Identify in this diagram the bromine radical species (a bromine atom has 35 electrons).
- 13.2 Identify in this mechanism two catalytic cycles for ozone loss.
- 13.3 This mechanism also decreases the ozone production efficiency (OPE) per unit NO_x . Explain why.
- 13.4 Critical to the importance of bromine chemistry is maintaining high concentrations of bromine radicals. At equilibrium, most of the bromine in the above mechanism would be present as HBr, which is the only long-lived non-radical reservoir. It is thought that regeneration of bromine radicals is mainly driven by the following reaction taking place in aerosols:



- Explain briefly why reaction (11) would regenerate bromine radicals.
- 13.5 If reaction (11) is fast enough it could trigger a “bromine explosion” where the concentration of bromine radicals grows catalytically. Consider the following condensed mechanism in which α is the fraction of Br atoms converted to HOBr by reactions (2+5), and β is the fraction of HOBr molecules converted to Br_2 by reaction (11):

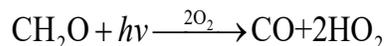
- 1'. $Br \rightarrow HOBr$ yield α (reactions 2+5)
- 2'. $Br \rightarrow HBr$ yield $(1-\alpha)$ (reaction 9)
- 3'. $HOBr \rightarrow 2Br$ yield β (reaction 11+4)
- 4'. $HOBr \rightarrow Br$ yield $(1-\beta)$ (reaction 6)

Draw a diagram for this condensed mechanism. Identify the catalytic reaction sequence that produces a bromine explosion. Show that a condition for this bromine explosion to take place is $\beta > \frac{1}{\alpha} - 1$.

CHAPTER 12: OZONE POLLUTION

1. Short questions

- 1.1 Surface ozone in urban air is maximum in the afternoon and minimum at night. Explain why.
- 1.2 NO_x is emitted from combustion sources mostly as NO , but there is also a small fraction emitted as NO_2 . Diesel cars have a larger NO_2/NO emission ratio than gasoline cars. For a given NO_x emission amount, does this make diesel cars contribute more to ozone pollution, or less?
- 1.3 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 NO_x -limited or VOC-limited. Why?
- 1.4 Imagine an atmosphere where the dominant HO_x radical sinks are the $\text{HO}_2 + \text{NO}_2$ and $\text{RO}_2 + \text{NO}_2$ reaction to form stable peroxy nitrates. Would ozone production in such an atmosphere be NO_x -limited or VOC-limited?
- 1.5 Observations at polluted sites show a linear relationship between $[\text{O}_3]$ and $[\text{NO}_y]$ - $[\text{NO}_x]$, where NO_y is the sum of NO_x and its oxidation products. The slope of this relationship provides an estimate of the ozone production efficiency (OPE) per unit NO_x . Why?
- 1.6 PAN formation decreases the ozone production efficiency in a NO_x source region but increases the ozone production efficiency on a global scale. Why?
- 1.7 Formaldehyde produced from the oxidation of VOCs can photolyze following



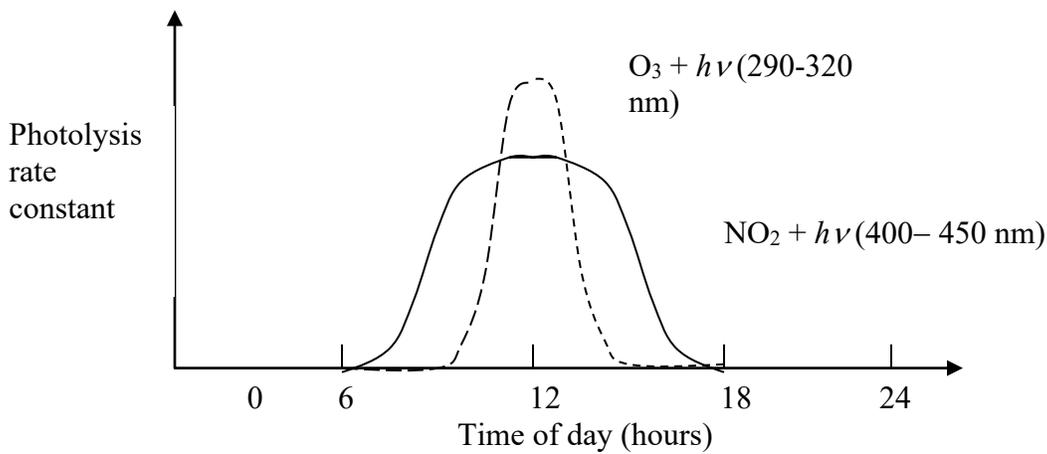
- This accelerates ozone production even in the NO_x -limited regime. Explain.
- 1.8 An important component of methane radiative forcing is the associated increase in tropospheric ozone. This increase in ozone when methane increases might seem odd because ozone production in the troposphere is generally NO_x -limited, not VOC-limited. But a major reason why increase in methane drives an increase in ozone even under NO_x -limited conditions is the formaldehyde photolysis reaction, $\text{CH}_2\text{O} + h\nu \xrightarrow{2\text{O}_2} \text{CO} + 2\text{HO}_2$. Explain why.
 - 1.9 Ozone production in urban air in winter is strongly VOC-limited. Under those conditions, an efficient way to produce ozone is by the NO_2 self-reaction taking place in aerosol particles: $\text{NO}_2 + \text{NO}_2 \xrightarrow{\text{H}_2\text{O}} \text{HNO}_2 + \text{HNO}_3$ followed by volatilization and photolysis of nitrous acid (HONO): $\text{HONO} + h\nu \rightarrow \text{OH} + \text{NO}$. Give two reasons why this mechanism would promote ozone formation.

2. An early-morning source of HO_x radicals in urban air

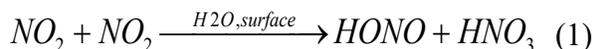
The build-up of ozone in urban areas over the course of the day is strongly dependent on the availability of HO_x radicals during the morning hours. The

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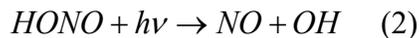
source of HO_x radicals from ozone photolysis is slow in early morning, as shown in the diagram below which compares the rate constants for NO₂ photolysis and O₃ → O(¹D) photolysis as a function of time of day:



- 2.1 Explain why O₃ photolysis does not increase as rapidly as NO₂ photolysis following sunrise. [Hint: the optical depth of the atmosphere is much larger at 290-320 nm than at 400-450 nm]
- 2.2 An alternate urban source of HO_x radicals in early morning is nitrous acid (HONO). The mechanism for HONO production is thought to involve reaction of NO₂ on wet surfaces:



Loss of HONO is by photolysis, with a lifetime of only minutes in the daytime:



Sketch qualitatively the diurnal variation of the HONO concentration in urban surface air with time of day, taking into account the effects of both chemical loss and vertical mixing. Assume the NO₂ concentration to be constant.

- 2.3 Formation of HONO at night is thought to speed up the production of urban ozone in the early morning hours by switching the chemical regime for ozone production from NO_x-saturated to NO_x-limited. Explain why.
- 2.4 It has been proposed that additional HONO generation in the daytime takes place by a branch of the atmospheric reaction of HO₂ with NO₂:

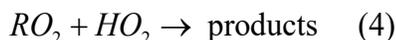
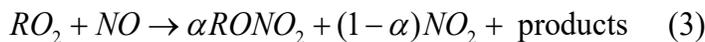
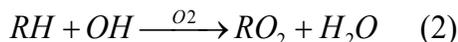
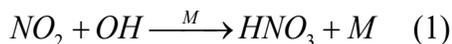
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This would have a very different effect on ozone. Write two radical cycles involving HONO production by (3) and loss by (2), assuming that OH reacts with CO and that NO reacts with either O₃ or with HO₂ (defining the two different cycles). Show that one cycle is null while the other is a catalytic ozone loss.

3. Production of organic nitrates from the oxidation of NO_x

Atmospheric oxidation of biogenic isoprene (denoted here as RH) in the presence of NO_x produces organic nitrates (RONO₂). This pathway competes with oxidation to nitric acid (HNO₃) as a sink for NO_x. Consider a box model for the continental planetary boundary layer (PBL) in summer with isoprene and NO_x emission denoted by E_{RH} and E_{NO_x} in units of molecules cm⁻³ s⁻¹, and the following mechanism:



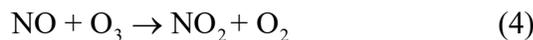
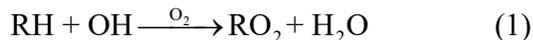
Assume that the “products” do not participate in further chemistry. Further assume that [OH] and [HO₂] are known, that [RO₂] can be deduced from steady state in the above mechanism, that the NO₂/NO concentration ratio is fixed such that [NO₂]/[NO] = β, and that isoprene and NO_x are in steady state between emission and chemical loss. The coefficient α < 1 in reaction (3) is the yield of RONO₂ from that reaction. We consider in this problem two limiting cases: a “high-NO_x” regime defined by rate(3) >> rate(4), and a “low-NO_x” regime defined by rate(3) << rate(4). Denote k_i as the rate constant (cm³ molecule s⁻¹) of reaction i .

- 3.1 Let Y represent the yield of RONO₂ from the oxidation of NO_x. Show that $Y = \alpha E_{RH}/E_{NO_x}$ in the high-NO_x regime.
- 3.2 Show that $Y = 1/(1 + \gamma/E_{RH})$ in the low-NO_x regime where γ is a combination of rate constants and known concentrations.
- 3.3 Plot Y vs. E_{RH} in both regimes. Show that Y is always larger in the low-NO_x regime than in the high-NO_x regime.

4. Ozone production efficiency

When ozone production is in the NO_x-limited regime, an important quantity used to project the benefit of NO_x emission controls is the ozone production efficiency per unit NO_x oxidized (OPE). Consider the following simplified mechanism for ozone

smog production involving the oxidation of a hydrocarbon (RH) in the presence of NO_x :



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)

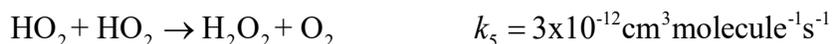
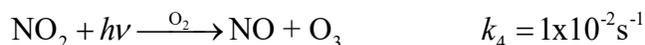
- 4.1 Show that $\text{OPE} = k_1[\text{RH}]/(k_5[\text{NO}_2])$.
- 4.2 It is more useful to express the OPE as a function of $[\text{NO}_x]$ rather than as a function of $[\text{NO}_2]$ because of the rapid cycling between NO and NO_2 . Derive an expression for the $[\text{NO}_2]/[\text{NO}_x]$ ratio as a function of $[\text{O}_3]$ 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_x emission controls for reducing ozone levels?
- 4.3 An alternate branch for reaction (2) produces a stable organic nitrate RONO_2 which is eventually removed by deposition:



Show that if this reaction dominates NO_x loss (that is, if (2') is much faster than (5)), then the OPE is a constant.

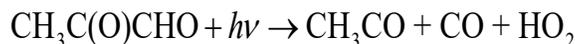
5. Isoprene effect on the ozone production efficiency

Isoprene (C_5H_8) 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_x :



and a typical atmosphere for the U.S. in summer containing 1×10^{10} molecules cm^{-3} isoprene, 1×10^{10} molecules cm^{-3} NO_x , 1×10^{12} molecules cm^{-3} ozone, and 5×10^8 molecules cm^{-3} HO_2 , with an air density of 2.5×10^{19} molecules cm^{-3} . 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.

- 5.1 Calculate the $[\text{NO}]/[\text{NO}_2]$ and $[\text{HO}_2]/[\text{OH}]$ concentration ratios.
- 5.2 Calculate the rates of the individual reactions and verify that (5) and (6) are indeed slow relative to the others.
- 5.3 For the conditions above, is ozone production in the NO_x -limited or NO_x -saturated regime? Briefly explain.
- 5.4 Show that the ozone production efficiency (OPE) per unit NO_x oxidized is 67 for these conditions. If isoprene emission were to increase, would the OPE increase or decrease? Briefly explain.
- 5.5 In fact the “products” of isoprene oxidation are not inert. One important product is methylglyoxal, $\text{CH}_3\text{C}(\text{O})\text{CHO}$, which photolyzes as follows:



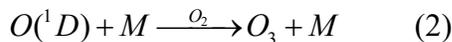
Inclusion of this reaction in mechanism (1)-(6) will increase the ozone production *rate* but not the OPE; briefly explain why.

- 5.6 Photolysis of methylglyoxal could actually decrease the OPE by converting NO_x to PAN; write the corresponding reactions and briefly explain why this would decrease the OPE.

6. A radical chemistry explosion?

Photolysis of formaldehyde (CH_2O) to produce HO_x radicals is called a *branching reaction* in the HO_x catalytic chain because it adds HO_x radicals as part of the propagation cycle. Such amplification could conceivably lead to an explosive runaway production of HO_x and we examine here if this can happen in the atmosphere. Throughout this problem, denote k_i as the rate constant of reaction (i).

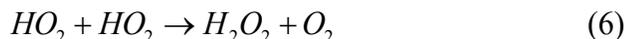
- 6.1 The HO_x radical chain is initiated by the photolysis of ozone in the presence of water vapor:



Let $P(\text{HO}_x)$ represent the source of HO_x radicals from reactions (1)-(3). Express $P(\text{HO}_x)$ as a function of the concentrations of O_3 , H_2O , and M.

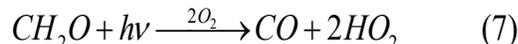
- 6.2 Consider now the following simplified schematic for the subsequent HO_x propagation and termination steps:

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Based on the mechanism (1)-(6), derive an equation for the OH concentration as a function of $P(HO_x)$, $[CH_4]$, and $[NO]$, assuming efficient HO_x cycling. You should find that OH concentrations increase as $[NO]$ increases and as $[CH_4]$ decreases.

- 6.3 The effect of methane on HO_x chemistry is complicated by the photolysis of CH_2O , producing HO_x radicals:



Write the HO_x steady-state equation to include the source from (7), assuming CH_2O to also be at steady state. Show that this steady-state equation always has a positive solution for $[HO_2]$, meaning that the system remains stable (no explosion). Show also that under these conditions $[OH]$ is still inversely dependent on $[CH_4]$ even though (7) provides a source of HO_x . Explain qualitatively why that is.

- 6.4 Explosive conditions can however arise in the NO_x -saturated regime, when the loss of HO_x is not by reaction (6) but instead by reaction of NO_2 with OH:



Write a steady-state equation for HO_x using (8) instead of (6) as HO_x sink. Show that the stability of the system depends on the relative abundance of CH_4 and NO_2 .

- 6.5 An alternate sink for CH_2O is reaction with OH. Without doing any calculations, explain why this alternate sink would help to stabilize HO_x concentrations in the NO_x -saturated regime.

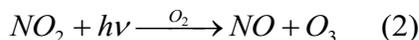
7. An ozone explosion?

The textbook explains that ozone production in the troposphere has two limiting regimes, NO_x -limited and NO_x -saturated, with different dependences for the ozone production rate $P(O_3)$:

$$P(O_3) \sim [O_3]^{1/2}[H_2O]^{1/2}[NO] \quad NO_x \text{-limited}$$

$$P(O_3) \sim [O_3][H_2O][CO]/[NO_2] \quad NO_x \text{-saturated}$$

In both regimes we see that $P(O_3)$ has a positive dependence on $[O_3]$. One could expect this positive feedback to lead to explosive accumulation of ozone. In fact, such explosive accumulation does not take place because of the null cycle controlling NO/NO_2 partitioning:



- 7.1 By expressing $P(O_3)$ as a function of $[NO_x]$ and assuming that reactions (1)-(2) are in steady state and control NO/NO₂ partitioning, show that the dependence of $P(O_3)$ on $[O_3]$ in the NO_x-limited regime eventually becomes negative when $[O_3] \gg k_2/k_1$.
- 7.2 There is no such stabilization in the NO_x-saturated regime. However, as $[O_3]$ becomes sufficiently high the regime must eventually switch from NO_x-saturated to NO_x-limited. Explain qualitatively why. [Hint: an increase in $[O_3]$ drives an increase in $[HO_x]$ (explain why), and as $[HO_x]$ increases the atmosphere is more likely to be NO_x-limited (explain why)].

8. Ozone production efficiency and diesel cars

Gasoline cars emit almost all of their NO_x as NO, but diesel cars emit a large fraction of their NO_x as NO₂. Here we consider the consequences for tropospheric ozone formation. Consider the following chemical mechanism for NO_x cycling and loss:

1. $NO + HO_2 \rightarrow NO_2 + OH$
2. $NO + O_3 \rightarrow NO_2 + O_2$
3. $NO_2 + h\nu \xrightarrow{O_2} NO + O_3$
4. $NO_2 + OH + M \rightarrow HNO_3 + M$

Assume that a fraction α of NO reacts by (1) and the remaining fraction $(1-\alpha)$ reacts by (2); that a fraction β of NO₂ reacts by (3) and the remaining fraction $(1-\beta)$ reacts by (4). Assume NO and NO₂ to be in steady state.

- 8.1 Assume that emission is solely as NO. Draw a diagram showing the source, cycling, and sink of the NO_x radicals. Label the reaction pathways with α , $1-\alpha$, β , $1-\beta$.
- 8.2 An emitted NO molecule can react by either of the four combinations (1)+(3), (1)+(4), (2)+(3), or (2)+(4). Give the probabilities for each of these four combinations, whether they produce or lose ozone, and whether they recycle NO or convert it to HNO₃. Show that the resulting net ozone production per NO molecule reacted is $P - L = \alpha + \beta - 1$.
- 8.3 If NO is recycled it can further react by the above combinations until it is eventually converted to HNO₃. Show that the net ozone production $P - L$ per NO molecule emitted is

$$P - L = (\alpha + \beta - 1)(1 + \beta + \beta^2 + \dots) = \frac{\alpha + \beta - 1}{1 - \beta}$$

- 8.4 Consider now a car that emits all its NO_x as NO₂. Show by the same reasoning that the net ozone production per NO₂ molecule emitted is

$$P - L = \frac{\alpha\beta}{1 - \beta}$$

- 8.5 Show by difference that there is $1-\alpha$ more ozone produced per emitted NO_2 than per emitted NO . Explain briefly your result.

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 N_2O_5 hydrolysis as a sink of NO_x in the troposphere. Why?
- 1.3 Organic acids are emitted by the biosphere and are also produced in the atmosphere from oxidation of VOCs. The most abundant organic acids in the atmosphere are formic acid ($pK_a = 3.8$) and acetic acid ($pK_a = 4.8$), where K_a denotes the acid dissociation constant. On a per mole basis, and assuming the same Henry's law solubility for formic and acetic acids, which of these two acids would most affect the pH of rainwater?
- 1.4 Liming of lakes by addition of limestone (CaCO_3) is a practical corrective solution to prevent acidification of lakes. Consider a small 1 km^2 lake receiving 1 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 g mole^{-1})
- 1.5 How do emissions from agriculture affect (1) stratospheric ozone, (2) greenhouse warming, (3) acid rain, (4) nitrogen deposition? Give an example for each effect.

2. Sulfuric vs. sulfurous acid

Sulfuric acid produced by oxidation of SO_2 is a major component of acid rain. However, dissolved SO_2 is an acid too (sulfurous acid), which may make one wonder about the actual importance of SO_2 oxidation as a source of acidity. We examine this issue here. The relevant equilibria for SO_2 dissolution and dissociation in cloudwater are:



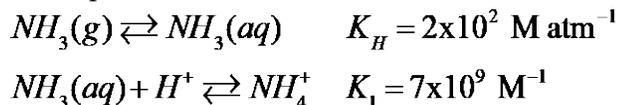
- 2.1 Calculate the pH of a droplet of pure water at equilibrium with a typical $p_{\text{SO}_2} = 1 \times 10^{-8} \text{ atm}$ for a polluted atmosphere. [Hint: ignore SO_3^{2-} and OH^- in the charge balance calculation, and verify the correctness of this assumption at the end]. You should find a pH value of 4.9. Since the dominant form of sulfur in solution is HSO_3^- , conclude as to the effect on pH of oxidizing this sulfur to SO_4^{2-} .

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- 2.2 A far more important effect has to do with sulfur dissolution. Consider a cloud with a typical liquid water content $L = 1 \times 10^{-6}$ cm³ liquid water per cm³ of air and temperature $T = 280$ 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 SO₂(g) vs. dissolves in the cloudwater phase as HSO₃⁻. [Hint: you will need to convert the SO₂ and HSO₃⁻ concentrations to common measures]. You should find that most of the SO₂ remains in the gas phase.
- 2.3 Oxidation of dissolved HSO₃⁻ to sulfate thus pushes gas-phase sulfur into the aqueous phase, greatly increasing acidity. For the conditions in question 2 and an initial $p_{SO_2} = 1 \times 10^{-8}$ 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.

3. Scavenging of ammonia by precipitation

Ammonia is efficiently scavenged by rain but this is very much determined by the rain pH. The relevant equilibria are



- 3.1 Consider a cloud with liquid water content L (liters of water per liter of air) at a temperature T (K). Let $()$ denote concentration in units of moles per liter of air, $[]$ denote concentration in units of moles per liter of water (M). We define the fraction F of ammonia scavenged by the cloud as

$$F = \frac{(NH_3(aq)) + (NH_4^+)}{(NH_3(g)) + (NH_3(aq)) + (NH_4^+)}$$

Show that

$$F = \frac{1}{1 + \frac{1}{LRTK_H(1 + K_1[H^+])}}$$

where $R = 8.2 \times 10^{-2}$ liters atm⁻¹ mol⁻¹ K⁻¹ is the gas constant.

- 3.2 Assuming typical values $L = 1 \times 10^{-7}$ and $T = 278$ K, determine the pH values for which $F = 0.1$, $F = 0.5$, $F = 0.9$. Plot qualitatively the shape of F as a function of pH over the pH range from 0 to 14. In the absence of atmospheric acids (i.e., if ammonia dissolved in pure water), would ammonia be efficiently scavenged?

4. Sulfate-nitrate-ammonium aerosol chemistry and acid rain over the US

Emissions of SO₂, NO_x, and NH₃ in the contiguous US are 5 Tg S a⁻¹, 6 Tg N a⁻¹, and 3 Tg N a⁻¹ respectively. The contiguous US has an area of 8 × 10⁶ km² and it rains on average 2 mm d⁻¹. Assume in this problem that the emissions are horizontally uniform over the US, that 50% of both SO₂ and NO_x are oxidized

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over the US to H_2SO_4 and HNO_3 (the rest is removed by dry deposition), and that H_2SO_4 , HNO_3 , and NH_3 are removed solely by wet deposition over the US.

- 4.1 Is ammonium nitrate aerosol formed in this system? Is there excess $\text{HNO}_3(\text{g})$ or $\text{NH}_3(\text{g})$ present?
- 4.2 Calculate the pH of the precipitation over the contiguous US resulting from the dissolution of H_2SO_4 , HNO_3 , and NH_3 . You should get a value of 4.6.
- 4.3 Consider a future where NH_3 emissions are double those at present while SO_2 and NO_x emissions remain the same. How would your answer to question (1) change?
- 4.4 Would we still have “acid rain” (as defined by $\text{pH} < 5$) under this future? Considering that plants take up NH_3 , not NH_4^+ , would net H^+ input to ecosystems decrease? Conclude as to whether increasing NH_3 emissions is an effective approach for solving the acid rain problem.

CHAPTER 14: AEROSOL CHEMISTRY

1. Short questions

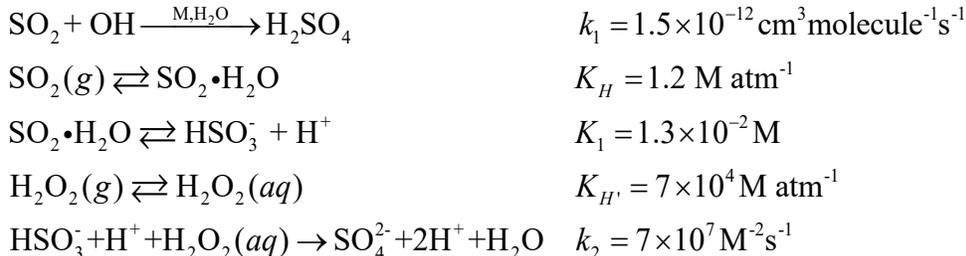
- 1.1 Air quality managers faced with an ammonium nitrate PM_{2.5} pollution problem can choose to reduce either NO_x or ammonia emissions. How can they make this choice in an informed way?
- 1.2 It has been argued that decreasing SO₂ emissions to decrease aerosol sulfate could result in an increase in aerosol nitrate, increasing in fact the total aerosol mass concentration. Explain the reasoning.
- 1.3 When sulfate is in excess of total ammonia, we saw that the effective way to decrease SNA PM_{2.5} was through SO₂ emission controls. But how about controlling ammonia emissions? Show that this would also decrease SNA PM_{2.5} but would be far less effective. Why? [hint: think of the difference in molecular weights between sulfate and ammonium]
- 1.4 Would you expect sulfate concentrations in polluted regions to be highest in summer or in winter?
- 1.5 Volcanic eruptions inject massive amounts of SO₂ to high altitudes. That SO₂ can be transported for weeks in the atmosphere before being oxidized, unlike SO₂ emitted near the surface which is oxidized within days. Why the difference?
- 1.6 Particle nucleation is observed only during daytime, why?
- 1.7 In the aqueous-phase model for SOA formation, we saw that controlling anthropogenic SO₂ emission would result in decreasing biogenic SOA by decreasing aerosol water content and acidity. In the organic-phase model for SOA formation, a different kind of anthropogenic emission control would decrease biogenic SOA. What is it?
- 1.8 Uptake of glyoxal by aqueous aerosols and cloud starts with hydration to the tetrol form CHOCHO(g) = C₂(OH)₄(aq) with Henry's law constant $K_H = [C_2(OH)_4]/p_{CHOCHO} = 4 \times 10^5 \text{ M atm}^{-1}$. In a typical cloud with liquid water content $L = 1 \times 10^{-4}$ liters water per liter of air, what fraction of total atmospheric glyoxal is partitioned as tetrol into the cloudwater? And what happens when the cloud evaporates and the aerosol liquid water content decreases to $L = 1 \times 10^{-9} \text{ cm}^3 \text{ water per cm}^3 \text{ of air}$?

2. Oxidation of SO₂ to sulfate

We show in this problem that in-cloud oxidation by H₂O₂ is the dominant pathway for SO₂ oxidation and allows for sulfate to be produced within the SO₂ 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⁻¹. SO₂ emitted in the airshed can be removed by ventilation, dry deposition ($k_d = 2 \times 10^{-6} \text{ s}^{-1}$), gas-phase

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oxidation by OH, and in-cloud aqueous-phase oxidation by H₂O₂. We examine in this problem the different pathways for SO₂ loss and the consequences for sulfate formation. Assume gas-phase concentrations [OH] = 1 × 10⁶ molecules cm⁻³ and [H₂O₂] = 1 ppb. Further assume $p = 900$ hPa and $T = 280$ K. You will need the following information:

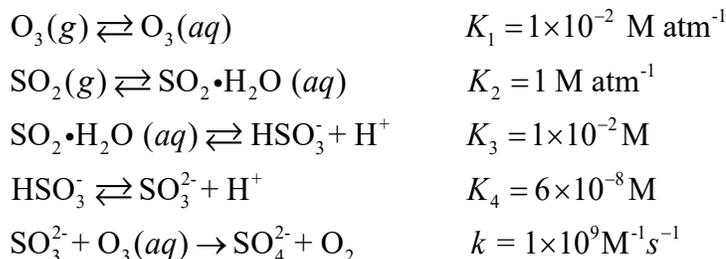


- 2.1 Consider first a cloud-free atmosphere, thus ignoring the in-cloud oxidation of SO₂ by H₂O₂(aq). Show that the SO₂ lifetime in the U.S. airshed is 2.1 days and that only 27% of emitted SO₂ produces sulfate within the U.S. airshed.
- 2.2 Clouds can greatly speed up the conversion of SO₂ to sulfate through oxidation by H₂O₂(aq). Consider a cloudy air parcel with a typical liquid water content $L = 1 \times 10^{-7}$ cm³ water per cm³ air. Show that SO₂ has a lifetime of only 1.7 hours against loss by aqueous-phase reaction with H₂O₂(aq) in that air parcel.
- 2.3 Clouds occupy typically 10% of the U.S. airshed, so that the corresponding lifetime of SO₂ in the airshed against in-cloud aqueous-phase oxidation is 17 hours. Show that 81% of the emitted SO₂ is now oxidized to sulfate within the U.S. airshed.
- 2.4 A critical assumption in our calculation is that the H₂O₂ concentration is not significantly depleted in cloud by oxidation of SO₂. 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 H₂O₂ production].
- 2.5 A second critical assumption in our calculation is that the SO₂ 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 SO₂, and the ensuing production of sulfate aerosol has important radiative effects on climate. We examine here the role of sea-salt aerosol in oxidizing SO₂ 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 SO₂ in the marine atmosphere. We focus on the fate of SO₂.

- 3.1 In most current atmospheric models the sinks for SO₂ in the marine atmosphere are (a) deposition to the ocean, (b) oxidation by H₂O₂ in clouds, and (c) gas-phase oxidation by OH. Assume that the atmospheric lifetimes for SO₂ against each of these sinks are (a) $\tau_{dep} = 1$ d, (b) $\tau_{cloud} = 1$ d, (c) $\tau_{OH} = 5$ d. Deduce the overall atmospheric lifetime of SO₂ and the fraction that is oxidized in the atmosphere to produce sulfate aerosol.
- 3.2 Oxidation of SO₂ 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 m³ air represent the fraction of the MBL volume occupied by sea salt aerosols. Show that the lifetime τ_{salt} of SO₂ against oxidation in sea salt aerosols is given by

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

- where p_{O_3} is the partial pressure of ozone, $[H^+]$ is the aerosol H⁺ concentration, R is the gas constant, and T is temperature. Explain briefly the dependence on $[H^+]^2$. For typical values of $p_{O_3} = 40 \times 10^{-9}$ atm and $T = 300$ K, calculate τ_{salt} at pH 5 and pH 8.
- 3.3 Sea salt aerosols when emitted have the same 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 τ_{salt} calculated in question (2), show that the potential of sea salt aerosols as sinks for SO₂ is limited by their alkalinity.
- 3.4 The global source of alkalinity emitted from the ocean as sea salt aerosols is 3×10^{11} eq a⁻¹. The global source of DMS is 20 Tg S yr⁻¹. Deduce the fraction of DMS-derived SO₂ 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 NO_x is incorporated into the aerosol. Consider an air parcel at $T = 290$ K containing a fixed gas-phase HNO₃(g) concentration of 1 ppbv at 1 atm in equilibrium with an otherwise pure-water aerosol. The relevant equilibria are:



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- 4.1 Calculate the pH of the resulting aerosol. You should find $\text{pH} = 1.3$. Is aerosol nitrate present mainly as 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 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.

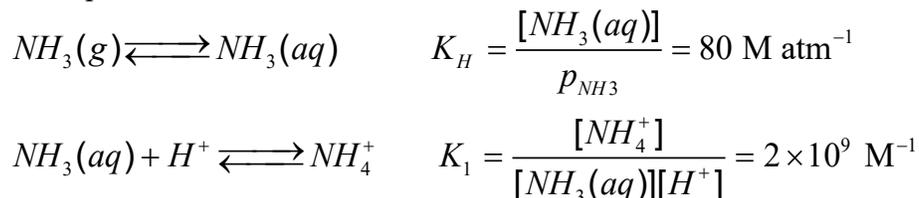
5. The sulfate-nitrate-ammonium aerosol system

Consider a box model for the US atmosphere including emissions of SO_2 , NO_x , and NH_3 . Denote these emissions as E_{SO_2} , E_{NO_x} , E_{NH_3} in units of moles per year. Assume that all emitted SO_2 is converted to sulfate inside the box, that all emitted NO_x is converted to 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 NH_3 and not by the supply of NO_x .
- 5.3 Under the conditions of 5.2, show that decreasing SO_2 emissions will actually cause an *increase* in aerosol mass concentrations due to formation of aerosol nitrate.

6. Partitioning of ammonia into aerosols and clouds

Consider the following equilibria for uptake of gaseous ammonia in aqueous aerosol particles and clouds:



Let L [liters of water per liter of air] denote the liquid water content of the air.

- 6.1 Show that $[\text{NH}_3(\text{aq})]$ is negligibly small compared to $[\text{NH}_4^+]$ for typical cloud pH values found in the atmosphere. We neglect $[\text{NH}_3(\text{aq})]$ in what follows.
- 6.2 Show that the fraction f of total atmospheric ammonia present in the aqueous phase is given by

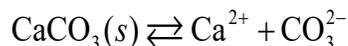
$$f = \frac{\{\text{NH}_4^+\}}{\{\text{NH}_3(\text{g})\} + \{\text{NH}_4^+\}} = \frac{1}{1 + \frac{1}{LRTK_H K_1 [\text{H}^+]}}$$

where the concentrations in $\{ \}$ are in units of moles per liter of air, T is the temperature in K, and $R = 8.31 \times 10^{-2} \text{ atm liter mol}^{-1} \text{ K}^{-1}$ is the ideal gas constant.

- 6.3 Find the pH at which $f = 0.5$ for a typical cloud water content $L = 1 \times 10^{-6}$ and with $T = 280 \text{ K}$. What do you conclude about the scavenging efficiency of ammonia by clouds and rain?
- 6.4 Find the pH at which $f = 0.5$ for a typical non-cloud aerosol water content $L = 1 \times 10^{-10}$ and with $T = 280 \text{ K}$. From this result, show that ammonia will be efficiently taken up by an aqueous sulfuric acid aerosol ($\text{pH} < 0$) but will not be efficiently taken up by a neutralized aqueous ammonium sulfate aerosol.

7. Mixing of dust and SNA aerosols

- 7.1 Formation of sulfate-nitrate-ammonium (SNA) aerosols can be limited by ammonia emissions under certain conditions. Briefly describe the conditions (chemical regime) under which this happens.
- 7.2 Consider that we are in such a chemical regime and that we decrease ammonia emissions in order to decrease $\text{PM}_{2.5}$ pollution. Eventually, as ammonia emissions get low enough, we will exit that regime. When that happens, should we switch to decreasing SO_2 emissions or to decreasing NO_x emissions in order to further decrease $\text{PM}_{2.5}$?
- 7.3 Mixing of SNA aerosols with calcium carbonate (CaCO_3) dust particles may affect the limitation by ammonia. Consider a CaCO_3 particle mixing with an aqueous SNA particle. The CaCO_3 dissociates following



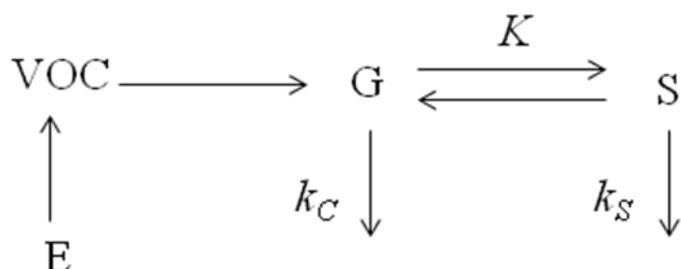
and the resulting carbonate ion⁻ volatilizes from the particle. Explain how this volatilization takes place.

- 7.4 By contrast, calcium is not volatile and remains in the particle as Ca^{2+} . If sufficient Ca^{2+} is present, then SNA formation will be limited by NO_x emission rather than by ammonia emission. Explain why.

8. 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 ($\text{molecules cm}^{-3} \text{ s}^{-1}$) is the VOC emission rate; VOC oxidation produces a gas-phase species G that partitions in thermodynamic equilibrium with S; k_C (s^{-1}) is the rate constant for gas-phase chemical loss of G; and k_S (s^{-1}) is the rate constant for deposition of S. The thermodynamic equilibrium constant K ($\text{cm}^3 \text{ molecule}^{-1}$) 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^3 of air, and $n_o = [P] + [S]$ is the total concentration of organic aerosol.

- 8.1 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]
- 8.2 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 $[P]$.
- 8.3 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?
- 8.4 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.

9. 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.

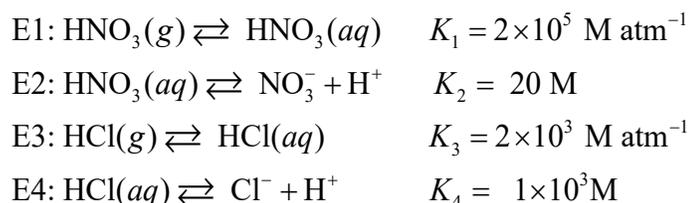
- 9.1 Glyoxal has mean atmospheric lifetimes of 2 hours against photolysis, 8 hours against oxidation by OH, and 8 hours against uptake by aqueous particles to form aerosol. What fraction of atmospheric glyoxal will form aerosol?
- 9.2 Isoprene emission in the U.S. in summer is estimated to be $5 \times 10^{11} \text{ molecules cm}^{-2} \text{ s}^{-1}$. 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

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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.

10. Tropospheric chlorine chemistry

Sea salt aerosol is a large source of chlorine to the atmosphere. Part of that chlorine is removed quickly by aerosol deposition, but a fraction can volatilize to the gas phase as HCl through acid displacement by HNO_3 . This involves the following equilibria (equilibrium constants K) between the aqueous sea salt aerosol and the gas phase:

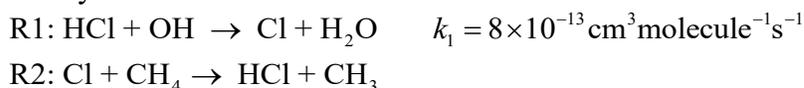


10.1 Show that the HCl partial pressure at equilibrium is given by

$$p_{\text{HCl}} = \frac{K_1 K_2 [\text{Cl}^-]}{K_3 K_4 [\text{NO}_3^-]} p_{\text{HNO}_3}$$

10.2 Typical observations in marine air show a HNO_3 concentration of 50 ppt, and that 20% of the Cl^- present in the freshly emitted sea salt aerosol has been displaced by NO_3^- . Show that the corresponding HCl concentration is 400 ppt.

10.3 HCl can lead to the loss of methane by producing chlorine atoms, which we assume here react solely with methane:

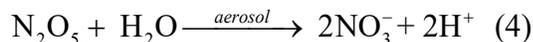
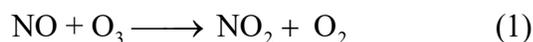


Calculate the lifetime of methane against loss by this mechanism in marine air by using the HCl concentration calculated above, $[\text{OH}] = 1 \times 10^6 \text{ molecules cm}^{-3}$, and 1800 ppb methane. You should find a value of about 200 years. Compare this value to what you know about the lifetime of methane. Is this mechanism an important methane sink?

11. Unexpected increase in nitrate aerosol as NO_x emissions decrease

Decreasing NO_x emissions in order to achieve a decrease in aerosol nitrate (NO_3^-) can in fact have an opposite impact under nighttime urban conditions. Under these conditions, aerosol nitrate formation takes place by the following mechanism:

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In this problem we assume that:

- NO_x emission is as NO ;
- There are no other reactions than (1)-(4);
- Reaction (1) is so fast that it can be considered instantaneous;
- Reaction (2) is sufficiently slow that it can be ignored as a sink for O_3 and NO_2 ;
- NO_3 and N_2O_5 are in steady state.

Consider a box model for the urban atmosphere initialized at sunset ($t = 0$) with concentrations $[\text{O}_3] = [\text{O}_3]_0$ and $[\text{NO}_x] = 0$, and featuring a steady NO_x emission E [molecules $\text{cm}^{-3} \text{s}^{-1}$] over the duration t_N of the night.

- 11.1 Show that the rate of aerosol nitrate production is given by $2k_2[\text{NO}_2][\text{O}_3]$, where k_2 is the rate constant of reaction (2).
- 11.2 Show that the O_3 concentration drops to zero at some point over the course of the night if $E > [\text{O}_3]_0/t_N$.
- 11.3 Show that the integrated production P of nitrate over the duration of the night is given by

$$P = 2 \int_0^{t^*} k_2[\text{NO}_2][\text{O}_3] dt = 2 \int_0^{t^*} k_2 E t ([\text{O}_3]_0 - E t) dt \quad \text{where } t^* = \min(t_N, [\text{O}_3]_0 / E)$$

- 11.4 In the regime $E \geq [\text{O}_3]_0 / t_N$, show that $P = \frac{k_2[\text{O}_3]_0^3}{3E}$.
- 11.5 In the regime $E \leq [\text{O}_3]_0 / t_N$, show that $P = 2k_2E \left([\text{O}_3]_0 \frac{t_N^2}{2} - E \frac{t_N^3}{3} \right)$ and that P is maximum for $E = \frac{3}{4} \frac{[\text{O}_3]_0}{t_N}$.
- 11.6 Sketch the resulting dependence of P on E . Explain qualitatively from the mechanism (1)-(4) why P can increase as E decreases. It is indeed a remarkable result that decreasing NO_x emission can increase aerosol nitrate!

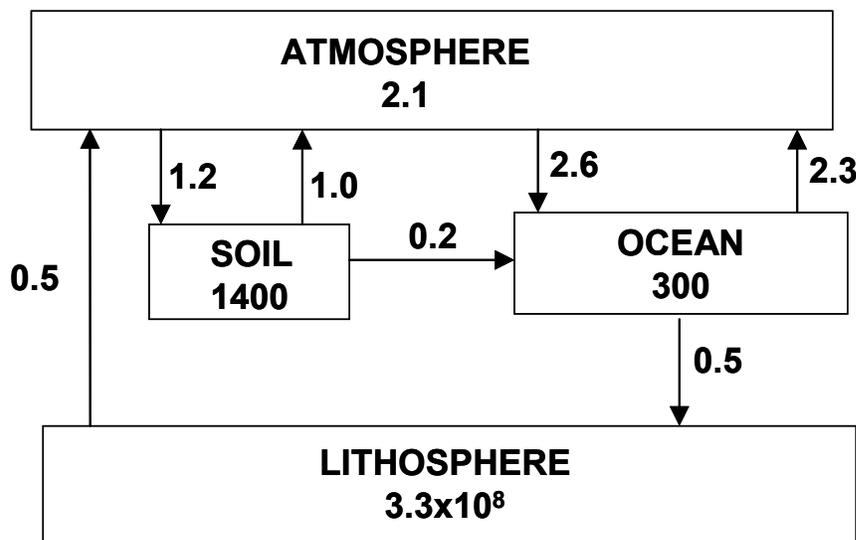
CHAPTER 15: BIOGEOCHEMICAL CYCLE OF MERCURY

1. Short questions

- 1.1 Even though mercury is a global pollutant, understanding *where* it gets oxidized in the atmosphere is critical for understanding its environmental impacts. Explain briefly why.

2. Global geochemical cycle of mercury

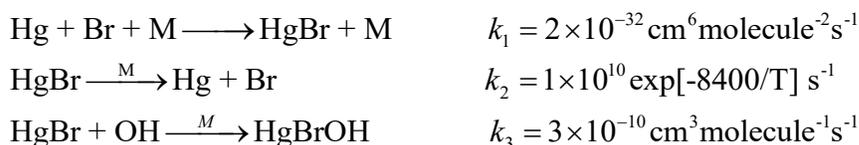
The diagram below shows an estimate of the natural steady-state global geochemical cycle of mercury. Inventories are in Gg and rates are in Gg a^{-1} .



- 2.1 Calculate the lifetime of mercury in each reservoir.
- 2.2 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.
- 2.3 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.

3. Mercury oxidation by Br atoms

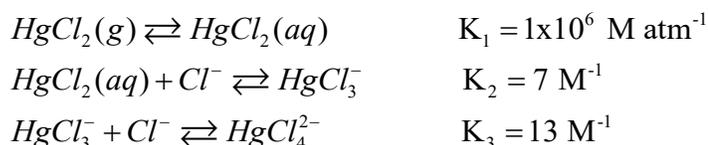
Oxidation by Br atoms has been proposed as an important pathway for oxidation of Hg(0) to Hg(II). We examine the rate of this process in surface air ($p = 1000$ hPa, $T = 298$ K) and in the upper troposphere ($p = 200$ hPa, $T = 200$ K). Assume in what follows a Br atom concentration $[\text{Br}] = 1 \times 10^5$ molecules cm^{-3} in surface air and $[\text{Br}] = 1 \times 10^6$ molecules 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 cm^{-3} . Consider the mechanism



- 3.1 Calculate the lifetimes of HgBr in surface air and in the upper troposphere. Identify the dominant HgBr loss pathway in each case.
- 3.2 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.

4. 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_2 . 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 $10 \mu\text{g}$ per m^3 of air. Assume that this sea salt is pure NaCl with solubility constant in water $K_s = [\text{Na}^+][\text{Cl}^-] = 36 \text{ M}^2$.

- 4.1 Show that the sea salt particles are aqueous and that $[\text{Cl}^-] = 3 \text{ M}$. [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]
- 4.2 Show that the liquid water content of the sea salt aerosol is $L = 3 \times 10^{-11} \text{ m}^3$ of water per m^3 of air. Use for this calculation $M_{\text{NaCl}} = 59 \text{ g mol}^{-1}$.
- 4.3 Calculate the fraction of total atmospheric Hg(II) that is incorporated in the sea-salt aerosol. Assume for this calculation $T = 300 \text{ K}$.

- 4.4 Would this fraction increase or decrease if the relative humidity rises to 95%? Briefly explain.