

Chapter 1: Measures of Atmospheric Composition (X1)

- (i) The mixing ratio of gas X in the atmosphere is constant at 1 ppmv (part per million by volume). What is the partial pressure P_X of X at 100 hPa?
(ii) Roughly speaking, how will the number density of X depend on height? Explain.
- The relative humidity does not change very strongly with height in the troposphere. But the partial pressure of water vapor in the atmosphere P_{H_2O} decreases very rapidly with height. What is the main reason for this rapid decrease?
- Draw a general plot of how the partial pressure of water vapor in the atmosphere P_{H_2O} depends on height in the troposphere.

Chapter 2: Atmospheric Pressure (X2)

Chapter 3: Simple Models (X3)

- Measurements indicate that N_2O is increasing at a rate of 0.3 % per year. Its current mixing ratio is 315 ppbv. Its mixing ratio in the preindustrial atmosphere was 285 ppbv. It is destroyed (mostly in the stratosphere) with an overall first order loss rate $k = 0.004 \text{ (year)}^{-1}$. Assume that this first loss rate k is constant. There are 1.8×10^{20} moles of air in the atmosphere.
 - Estimate the number of moles of N_2O emitted from the surface in the preindustrial atmosphere. (Hint: you can assume that N_2O sources and sinks were in balance.)
 - Estimate the current emission of N_2O from the surface (in moles per year).
 - If the current production were to stay constant, what would be the new steady state N_2O mixing ratio.
 - What is the main reason for the increased emission of N_2O into the atmosphere?
- This question involves setting up a two box model of the troposphere and stratosphere. The tropopause occurs at 150 hPa. The surface is at 1000 hPa. The first order rate constant for the transfer of mass from the troposphere into the stratosphere is $k_{TS} = 0.135 \text{ yr}^{-1}$.
 N_S : number of moles in the stratosphere
 N_T : number of moles in the troposphere
 - Solve for the first order rate constant for the transfer of moles from the stratosphere to the troposphere (k_{ST}).
 - The total number of moles in the troposphere and stratosphere is $N_a = 1.8 \times 10^{20}$. The mixing ratio of a CFC is 200 pptv in the troposphere and 150 pptv in the stratosphere. Solve for $N_{CFC,T}$ and $N_{CFC,S}$, the number of moles of the CFC in the troposphere and stratosphere respectively.
 - What is the rate of change of the CFC in the stratosphere (in pptv/year), taking into account transport from the troposphere, transport to the troposphere, and chemical loss. The first order loss rate for the chemical loss of the CFC in the stratosphere is $k_L = -0.1 \text{ year}^{-1}$.
 - If the CFC is increasing in the troposphere at a rate of 25 pptv/year, what is the rate of emission (in moles/year) of the CFC into the troposphere? Take into account transport to and from the stratosphere. Assume that there is no chemical destruction of the CFC in the troposphere.
- Assume the average pressure at the tropopause is 166 hPa and that the global average surface pressure is 1000 hPa. Define,
 M_T = mass of the troposphere
 M_S = mass of the stratosphere

Determine the ratio M_S/M_T .

(ii) Assume a two box model for the atmosphere. If the tropopause pressure does not change with time, and the transfer rate coefficient k_{ST} for transport of air from the stratosphere to the troposphere is 0.7 yr^{-1} , find k_{TS} , the first order rate coefficient for transfer of air from the troposphere to the stratosphere.

(iii) The stratosphere contains 90% of the total mass of ozone in the atmosphere. The atmosphere contains 5×10^{13} moles of ozone. Find the number of moles of ozone transported per year from stratosphere to the troposphere, and from the troposphere to the stratosphere.

(iv) The mean concentration of OH in the troposphere is $[OH] = 1.2 \times 10^6 \text{ molecules/cm}^3$. The reaction constant for the reaction of OH with methane is $2.6 \times 10^{-15} \text{ cm}^3/\text{molec} - \text{sec}$. What is the first order rate constant k_{CH_4} for the loss of methane via the OH reaction in the troposphere (in units of yr^{-1}).

(v) What is the lifetime of CH_4 in the troposphere with respect to transport into the stratosphere (in years)?

(vi) What is the lifetime of CH_4 in the troposphere with respect to reaction with OH (in years)?

(vii) The average mixing ratio of CH_4 in the troposphere is 1.7 ppmv (parts per million by volume.) Assume the two losses of CH_4 are OH attack and transport to the stratosphere. Assume the only CH_4 source is surface emission. Assume a mean tropopause pressure of 166 hPa, and that the mixing ratio of methane in the atmosphere is constant. Estimate the number of moles of methane emitted from the surface per year. (Hint: Find the number of moles in the troposphere.)

$$1 \text{ hPa} = 100 \text{ Pa} = 100 \text{ N/m}^2$$

$$\text{gravitational acceleration } g = 9.80 \text{ m/sec}^2$$

$$\text{radius of the earth } R = 6400 \text{ km}$$

$$\text{mean molecular weight of air } M_a = 28.96 \text{ g/mole}$$

4. Gas X is emitted entirely into the Northern Hemisphere. Let m_n the mass of X in the Northern Hemisphere and m_s the mass of X in the Southern Hemisphere. The first order exchange constant for the exchange of mass between the two hemispheres is $k = 0.9(\text{yr})^{-1}$. Gas X has a first order loss rate in the atmosphere of $k_l = 0.8(\text{yr})^{-1}$ in both hemispheres. Calculate m_n/m_s . (Ignore exchange with the stratosphere.) You can assume that X is in steady state in both hemispheres.

5. Assume that CFC-12 has an emission rate from the surface of $E = 4 \times 10^8 \text{ kg/year}$, and that the only removal mechanism from the troposphere is transport to the stratosphere. Assume the first order loss rate of CFC-12 in the stratosphere due to photolysis is $k_L = 0.05 \text{ yr}^{-1}$. Adopt the following conventions:

k_{ST} - first order rate constant for the transfer of air from stratosphere to the troposphere

k_{TS} - first order rate constant for the transfer of air from troposphere to the stratosphere

$M_{CFC,T}$ - mass of CFC-12 in the troposphere

$M_{CFC,S}$ - mass of CFC-12 in the stratosphere

k_L - first order chemical loss rate of CFC-12 in the stratosphere

(i) Write down an expression for the rate of change of $M_{CFC,T}$ that includes the processes mentioned above.

(ii) Write down an expression for the rate of change of $M_{CFC,S}$ that includes the processes mentioned above.

Assume:

$$k_{TS} = 0.135 \text{ yr}^{-1}$$

$$k_{ST} = 0.77 \text{ yr}^{-1}$$

(iii) Assume that the masses of CFC-12 in the troposphere and stratosphere are at steady state. Evaluate $M_{CFC,S}$.

(iv) What fraction of the total mass of CFC-12 in the atmosphere is in the stratosphere at steady state?

(v) Bonus question: what is the atmospheric lifetime of CFC-12 in the atmosphere (troposphere + stratosphere)?

6. Consider an urban area modeled as a square of size L with a height of h . A gas X is emitted into the box from the surface at a uniform rate of E ($\text{kg}/\text{m}^2\text{sec}$). X is removed from the box by a constant wind of strength U . The wind does not result in a flux of X into the box. The density of X in the box is ρ_X (kg/m^3). Assume that the density of X is uniform in the box. Call the total mass of X in the box m_X .

(i) What is the rate at which X is being emitted into the box (kg/sec)?

(ii) What is the rate at which X is being advected out of the box (kg/sec)?

(iii) Write down an equation for the rate of change of m_X .

(iv) What is the density of X (ρ_X) in the box at steady state?

7. What is dry deposition? Name two atmospheric constituents for which dry deposition can be an important sink.

Chapter 4: Atmospheric Transport (X4)

What is the residence time of an air parcel in the stratosphere? (About three years) What is the basic outline of the stratospheric circulation? What is the polar vortex? How does it influence the evolution of the Antarctic ozone hole? How does the ratio of the chemical lifetime of a species to the dynamical lifetime affect its distribution? The size of the region over which a chemical species is enhanced about a source region is roughly equal to the product of the species lifetime by the ambient winds.

1. What is the approximate typical residence time of an air parcel in the stratosphere?

2. What is the main reason ozone columns are higher in mid-latitudes than the tropics?

3. Plot the typical seasonal evolution of tropopause height from January to December at a Northern Hemisphere mid-latitude location. Indicate the typical maximum and minimum tropopause heights. Also plot on this figure how you would expect the ozone column to vary over a year.

4. Give an estimate for each timescale.

(i) Timescale for vertical overturning in the troposphere.

(ii) Timescale for interhemispheric exchange in the troposphere.

(iii) Timescale for parcel in the troposphere to go into the stratosphere.

(iv) Timescale for parcel in the stratosphere to go into the troposphere.

(v) Timescale for parcel to be dispersed in east-west direction.

(vi) Timescale for mixing within a hemisphere.

5. How does total ozone column respond to changes in tropopause height. Explain.

Chapter 5: The Continuity Equation (X5)

Chapter 6: Geochemical Cycles (X6)

- The preindustrial atmosphere contained sulfur compounds emitted by marine phytoplankton and volcanoes, and NO_x emitted by soils and lightning. These sources accounted globally to 1×10^{12} moles S/year and 1×10^{12} moles N/year, respectively. Assume that all the emitted sulfur and NO_x are oxidized in the atmosphere to H_2SO_4 and HNO_3 respectively, which are then scavenged by rain. Radius of the earth =
 - Estimate the mean concentrations (M) of SO_4^{2-} and NO_3^- in rain, assuming a global mean precipitation rate over the earth of 2 mm/day.
 - Assuming there was nothing else present to influence the acidity of rainfall, estimate the mean pH of rain in the preindustrial atmosphere.
 - In reality there was an additional important natural source of acidity to the background atmosphere. Specify what it was, and indicate the reactions by which it increased $[\text{H}^+]$.
 - There were also natural sources of alkalinity to the preindustrial atmosphere. Specify one and indicate the reactions by which it would have decreased $[\text{H}^+]$.
- When CO_2 dissolves in the ocean, it can assume one of the following three chemical forms: $\text{CO}_2 \cdot \text{H}_2\text{O}$, HCO_3^- , or CO_3^{2-} . Make a plot of the relative contribution of each of these three forms to the total $\text{CO}_2(\text{aq})$ as a function of ocean pH. Indicate on this diagram the current pH of the ocean, and therefore, the dominant form of $\text{CO}_2(\text{aq})$.
 - Fossil fuel emissions of CO_2 are increasing the concentration of dissolved CO_2 in the ocean. Is this expected to increase or decrease ocean pH? Explain using relevant chemical reactions.
 - This change in pH has an important impact on the ability of the ocean to uptake additional dissolved CO_2 . Explain.
- The CO_2 and O_2 cycles are strongly coupled.
 - Discuss one process which couples the two cycles on long (geological) time scales.
 - Discuss one process which couples the two cycles on short (seasonal) time scales.
 - Which process is more likely to exert greater control on the mean level of O_2 in the atmosphere. Explain.
- What is a mechanism by which CO_2 in the ocean mixed layer is removed to the deep ocean.
- What is one pathway by which N_2 in the atmosphere can enter the biosphere?
- What are two natural sources of NO_x to the atmosphere?
- We discussed in class why biomass does not exert a strong controlling influence on O_2 levels in the atmosphere. Over long timescales, what are the main sources and sinks of oxygen to and from the atmosphere?
- Atmospheric Oxygen O_2 shows a small seasonal variation. At what time of year would you expect oxygen concentrations to be a maximum. Explain. (Assume you are in the Northern Hemisphere).
 - Estimate the size of this seasonal variation (i.e. $\Delta\text{O}_2/\text{O}_2$ where ΔO_2 is the change in mixing ratio from minimum to maximum, and O_2 is the average value). The mean mixing ratio of O_2 in the atmosphere is 0.2. The seasonal variation in CO_2 is about 5 ppmv. Respiration and photosynthesis can be described by:

$$n\text{CO}_2 + n\text{H}_2\text{O} \leftrightarrow (\text{CH}_2\text{O})_n + n\text{O}_2$$
- The oxygen concentration of the atmosphere currently has a negative trend. Why?
- Nitrogen fixing bacteria play a special role in the nitrogen cycle. What do they do? (i.e. how do they interconvert nitrogen?)

10. (i) Do increasing atmospheric CO₂ concentrations increase or decrease the pH of the oceans? Explain using the relevant reactions.
(ii) Suppose some process were to decrease the pH of the oceans (i.e. increase the [H⁺] concentration.) Would this tend to drive CO₂ from the atmosphere into the ocean or from the ocean into the atmosphere? Explain using the relevant chemical equations.
11. What are two mechanisms by which O₂ is removed from the atmosphere?
12. What is a mechanism by which N₂ is removed from the atmosphere?
13. What is a mechanism by which CO₂ is removed from the surface mixed layer of the ocean?
14. Are increasing atmospheric CO₂ concentrations expected to increase or decrease the pH of the oceans? Explain with reference to the relevant reactions.
16. What are two ways in which carbon near the surface is transported to the deep ocean?
17. The CO₂ and O₂ cycles are strongly coupled.
(i) Discuss one process which couples the two cycles on long (geological) time scales.
(ii) Discuss one process which couples the two cycles on short (seasonal) time scales.
(iii) Which process is more likely to greater control on the mean level of O₂ in the atmosphere. Explain.
18. The oceans can, in principle, take up most of the CO₂ emitted into the atmosphere by fossil fuel burning. There are a variety of factors which inhibit ocean uptake of CO₂. Discuss one.
19. What are two gases emitted in volcanic plumes?
20. Define net primary productivity (NPP).
21. Does growth of corals (Ca²⁺ + CO₃²⁻ → CaCO₃(s)) cause atmospheric CO₂ to increase or decrease? Explain briefly.
22. What is a geological sink of O₂ from the atmosphere?

Chapter 7: The Greenhouse Effect (X7)

Chapter 8: Aerosols (X8)

1. What is a source of sulfate aerosols to the stratosphere?

Chapter 9: Chemical Kinetics (X9)

Estimating oxygen column above a certain pressure: The pressure at an altitude z , $p(z)$, is equal to the weight of the atmospheric column above that height per unit area. You have to go from pressure to mass per area, from mass per area to moles per area, then use the oxygen mixing ratio to get moles oxygen per unit area, then multiply by Avogadro's number to get molecules O₂ per unit area (molecule column amount). For oxygen you can always assume a constant mixing ratio of 0.2. The ozone mixing ratio is always height dependent.

$$p(z) = \frac{\text{Weight of air column above } z}{\text{area of column}}$$

Define $M(z)$ as the mass of the air column above z per unit area. g is the gravitational acceleration: $p(z) = M(z)g$. Define $N_{O_2}(z)$ as the number of O_2 molecules above a height per unit area. If $M(z)$ has units of $\frac{kg}{m^2}$, then

$$N_{O_2}(z) = M(z) \times \frac{1000 \text{ g}}{\text{kg}} \times \frac{1 \text{ mole air}}{28.964 \text{ g}} \times \frac{6.02 \times 10^{23} \text{ molec air}}{1 \text{ mole air}} \times \frac{0.21 \text{ molec } O_2}{1 \text{ molec air}} \times \frac{m^2}{10^4 \text{ cm}^2}$$

This will give you $N_{O_2}(z)$ in molecules O_2 per cm^2 . If $n_{O_2}(z)$ is the oxygen concentration as a function of height, then

$$N_{O_2}(z) = \int_z^\infty n_{O_2}(z) dz.$$

1. Assume that 1 percent of the incident top of the atmosphere solar flux at 300 nm reaches the ground. Also assume that the only significant absorber in the atmosphere at this wavelength is ozone, and that scattering can be neglected. The ozone absorption cross section at 300 nm is $34.3 \times 10^{-20} \text{ cm}^2$ per molecule. The solar zenith angle is 60° (from the vertical).

(i) What is the optical depth δ of the atmosphere at a solar zenith angle of 60° from the vertical? *The transmissivity T is transmitted flux divided by the incident. Here you are given $T = 0.01$. Use $T = e^{-\delta/\cos\theta}$. Solve for the optical depth given T and θ .*

(ii) What is the optical depth δ of the atmosphere for overhead sun? *Same as (i) except $\theta = 0$.*

(iii) What is the column ozone amount in molecules per cm^2 ? *The optical depth δ equals column amount times the molecular cross section. Make sure units consistent.*

(iv) What is the ozone column in Dobson Units? 1 Dobson Unit = 2.69×10^{16} molecules per cm^2 . *Just a unit conversion.*

2. Species X has an absorption cross section of $\sigma = 1 \times 10^{-20} \text{ cm}^2$ per molecule at a particular wavelength. Assume that at this wavelength, it is the only species which absorbs or scatters radiation. When the sun is at an angle of 30 degrees from the vertical ($\theta = 30^\circ$), 10 % of the solar radiation incident at the top of the atmosphere is absorbed before it reaches the ground. What is the column concentration of species X? (By column concentration N is meant the vertically integrated number of molecules per unit area above a particular point.)

4. The photolysis rates of NO_2 and NO_3 are almost independent of height. Explain.

5. Figure 2.5 in “Research Problems in Atmospheric Chemistry” can be primarily understood on the basis of absorption by oxygen and ozone. The oxygen absorption cross sections are given in Figure 3.3 and ozone cross-sections are given in Figures 3.4 and 3.5. Assume the atmosphere is isothermal at 280 K, oxygen is 21 percent of the atmosphere, and the ozone layer is 300 Dobson Unit thick at the ground, 200 Dobson at 20 km, and 50 Dobson at 30 km. 1 DU = 2.69×10^{20} molecules per m^2 . Assume a solar zenith angle of 60° , as has been done in the figure.

(i) Calculate the optical depth and fractional transmissions at 200 nm from ozone and oxygen at 20 and 30 km.

(ii) Which gas is more important?

(iii) Is it consistent with the figure?

(iv) Do the same at 250 and 300 nm.

(v) What is the reason for the “window” region at about 220 nm?

7. Show a plot of how the photolysis rate of a species like N_2O , which is destroyed by UV light, typically depends on height from the surface to 50 km.
8. (i) Suppose the transmissivity of the atmosphere at a particular wavelength due to an absorber is 0.01. What is the optical depth at that wavelength?
(ii) Suppose the concentration of the absorber in the atmosphere were doubled. What would be the new transmissivity?
9. Suppose the optical depth of the atmosphere at a particular wavelength is 3. what fraction of the sun's radiation at that wavelength would you expect to reach the surface?
12. The intensity of UV radiation at the surface, under clear sky conditions, is dependent on what two main variables. (*ozone column and solar zenith angle*).
13. Assume that 1 percent of the incident top of the atmosphere solar flux at 300 nm reaches the ground. Also assume that the only significant absorber in the atmosphere at this wavelength is ozone, and that scattering can be neglected. The ozone absorption cross section at 300 nm is 34.3×10^{-20} cm^2 per molecule. The solar zenith angle is 60° (from the vertical). 1 Dobson Unit = 2.69×10^{16} molecules per cm^2 . What is the ozone column in Dobson Units?
15. Species X has a constant mixing ratio of 100 ppbv in the atmosphere, i.e. $C_x = 1.0 \times 10^{-9}$. The absorption cross-section of X at 300 nm is 1.0×10^{-16} cm^2 /molecule.
Assume:
Pressure at the surface = $P_0 = 1.0 \times 10^5$ N/ m^2 .
gravitational acceleration = $g = 9.80$ m/ sec^2
Mean molecular weight of air = $M_a = 28.96$ g/mole
Avogadros number = $N_a = 6.02 \times 10^{23}$ molec/mole
(i) What is the total atmospheric column of X (in molec/ cm^2)?
(ii) What is the optical depth of X in the atmosphere at 300 nm?
(iii) If there are no other absorbers in the atmosphere at 300 nm, what fraction of the incoming solar radiation at 300 nm reaches the surface?
16. Suppose molecule A is dissociated by light with wavelengths less than 250 nm, while molecule B is dissociated by visible light. Roughly plot how the photolysis rates of A and B would depend on altitude.
17. The O_3 absorption cross-section at 300 nm is 34.3×10^{-20} cm^2 . The O_3 column is 8×10^{18} molec/ cm^2 . Assume the sun is directly overhead (ie. solar zenith angle of zero).
(i) What is the optical depth of the atmosphere due to O_3 at 300 nm?
(ii) What is the percentage increase in 300 nm flux at the surface if the O_3 column decreases by 5 %
?
18. Assume molecule A is photolyzed by visible light. Plot how you would expect its photolysis rate to depend on height in clear sky conditions. Assume molecule B is photolyzed by far UV light of about 200 nm. Plot how you would expect its photolysis rate to depend on height (roughly).
19. Species X is photolyzed mainly by photons with wavelengths of 280-300 nm. Species Y is photolyzed mainly by photons in the range 550-600 nm.
(i) Contrast how you would expect the photolysis rates of species X and Y to depend on height by drawing a schematic diagram.
(ii) Contrast how you would expect the photolysis rates of species X and Y to depend on solar zenith angle by drawing a schematic diagram.

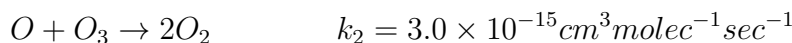
- (iii) What is a dominant physical process determining the actinic flux at the surface in the 280-300 nm range.
- (iv) What is an important physical process determining the actinic flux at the surface in the 550-600 nm range. *could say: aerosols, clouds, solar zenith angle, altitude, ozone from Cappuis ozone band.*
21. (i) What is the main atmospheric absorber of radiation between 100 and 242 nm?
(ii) What is the main atmospheric absorber of radiation between 242 and 350 nm?
22. (i) Give the expression by which photolysis rates (J values) are calculated. Identify all variables.
(ii) The J values of species with very fast photolysis rates (such as eg. NO₂ and NO₃) usually have very little height, or solar zenith angle, dependence. Explain.
23. Suppose at some wavelength the atmosphere has an optical depth of 2. What fraction of incident top of the atmosphere solar flux at this wavelength reaches the surface?
24. The absorption cross-section of species A and B are shown below.
(i) How would you expect the photolysis rate of species A to depend on height? Why?
(ii) How would you expect the photolysis rate of species B to depend on height? Why?

Chapter 10: Stratospheric Ozone (X10)

Stratospheric Ozone: Chapman ozone chemistry (S1)

1. The scheme for ozone production and destruction involving O_x species only is called the Chapman scheme.
(i) How is O_x produced in this scheme? What is the O_x production rate?
(ii) How is O_x destroyed in this scheme? Write out two O_x destroying cycles and specify the O_x destruction rate in terms of the relevant reactant concentrations and reactions constants.
(iii) What is a successful prediction of this scheme?
(iv) What is a failure of this scheme?
2. Ozone concentrations are largest near 30 km. Why do ozone concentrations decrease with height above 30 km, and decrease toward the surface?
3. Give two reasons why the concentration of atomic oxygen [O] increases rapidly with height in the stratosphere.
4. Give two reasons for the rapid increase in the O/O₃ ratio with height in the stratosphere.
5. (i) Why does O_x production go to zero at high altitudes?
(ii) Why does O_x production become small as you approach the surface?
6. Specify how many O_x are created (+) or destroyed (-) in the following reactions.
(i) $O + O \rightarrow O_2$
(ii) $O^1D + N_2 \rightarrow O + N_2$
(iii) $O_2 + h\nu \rightarrow O + O$
(iv) $O^1D + H_2O \rightarrow 2OH$
7. At an altitude of approximately 40 km, the temperature is 260 K, and the pressure is 3 hPa. Assume the set of reactions:





The rate constant given for the reaction between O and O₂ is the low temperature limit. A form of the ideal gas law is that the density of air (molec/m³) is given by

$$n_a = \frac{A_v P}{RT}$$

where A_v is Avogadro's number (6.023 × 10²³ molec/mole), P is pressure in Pa, R is the ideal gas constant (8.31 Jmol⁻¹K⁻¹) and T is temperature.

[O₂] ≈ 0.2 [M], where [M] is the total density (ie. [M] = n_a)

(i) Given this reaction scheme, determine the O/O₃ ratio. You may use family style approximations. (ie. instantaneous production and loss of a member of a family is dominated by reactions which interconvert family members). You may also make appropriate steady state assumptions.

Asking you to derive the O/O₃ ratio given in the lecture notes.

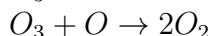
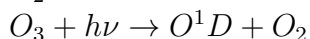
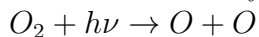
(ii) Find the O₃ concentration. (Hint: impose steady state in O_x)

Asking you to derive the O₃ expression given in the lecture notes.

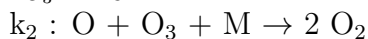
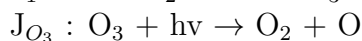
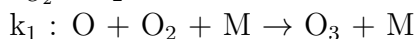
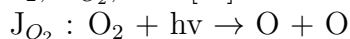
(iii) Convert the O₃ concentration to a mixing ratio in parts per billion (ppbv)

Use the expression given for n_a (i.e. the ideal gas law) to convert a concentration to a mixing ratio.

8. Indicate how many O_x are destroyed or produced by the following reactions.



9. (i) Derive the Chapman expression for the ozone concentration. You may make all necessary family style approximations. Write [O₂] = C_{O₂}[M], where [M] is the total number density of the atmosphere (sometimes called n_a). Your final answer should express [O₃] in terms of J_{O₂}, J_{O₃}, k₁, k₂, C_{O₂}, and [M]. Assume the following reactions:



Given in the lecture notes. Note that photolysis rates here labeled as J values but indicated by k's in the text.

(ii) Make a plot of the typical vertical variation of J_{O₂} as a function of height from the surface to 50 km.

Oxygen photolysis shown in the lecture notes and text. Photolysis rate near zero below 20 km since no flux with wavelength below 240 nm reaches these levels, due to overhead oxygen and ozone absorption. Photolysis rate converges to a constant value at high altitudes since so little overhead atmosphere and very little attenuation of top of the atmosphere solar flux.

(iii) Make a plot of the typical vertical variation of [O₃] as a function of height from the surface to 50 km as predicted by the Chapman expression. Explain the behavior at high and low altitudes.

Given in the lecture notes. As discussed in the notes, the ozone concentration from this expression goes to zero in the troposphere (or below 20 km) since oxygen photolysis zero. Goes to zero above 30 km, since $[M]$ goes to zero.

(iv) What is the main failure of the Chapman expression for $[O_3]$? Explain the reasons for this failure.

Discussed in the lecture notes: ozone too big since expression does not include all sinks.

10. (i) What are the sources and sinks of O_x in Chapman (oxygen only) chemistry.

(ii) Derive the Chapman expression for the ozone concentration using family style approximations.

11. What is the main reason O_3 concentrations decrease above 35 km?

12. What is the main failing of Chapman ozone chemistry (ie. O_x species only) when compared to observed ozone concentrations?

13. Why is there a stratospheric ozone layer? I.e. why does the production of ozone become small high up in the atmosphere, and why does it become smaller in the troposphere?

15. Using odd-oxygen chemistry alone, and suitable family style approximations, calculate the O/O_3 and O^1D/O_3 ratios at 20 and 40 km. Compare your answers with what you can estimate from page 199 of the JPL handouts.

16. Show that the O_2 photolysis source of O is indeed much smaller than the two O_3 photolysis sources at 20 and 40 km. That is, that rates of recycling between O_x family members are much larger than the rate of input into the family.

Stratospheric Ozone: Catalytic ozone destruction by HO_x, NO_x, ClO_x (S2)

1. (i) Assume that an air parcel in the stratosphere consists of the following gases *only*: O_2 , O_3 , O , O^1D , H_2O , N_2 , OH , and HO_2 . Draw a diagram showing the above species and the reactions between them. Use the list of all possible reactions on the accompanying pages. Ignore the photolysis of H_2O , but include the two photolysis channels of O_3 , and the photolysis of O_2 . Do not include reaction involving species not in the above list.

(ii) What is the source of ozone?

(iii) What are the sinks of ozone?

(iv) What is the source of HO_x ?

(v) What is the sink of HO_x ?

(vi) Derive an implicit expression for $[O_3]$ in terms of the J values, rate constants, and the concentrations of O_2 , N_2 , and H_2O . Do not try to solve this expression.

2. (i) Write out a chemical cycle involving NO_y and HO_x species which destroys HO_x . Point out the existence of competing reactions at some of the steps.

(ii) Write out a chemical cycle involving NO_y and HO_x species, and the N_2O_5 aerosol reaction, in which HO_x is created. Again, some of the steps will not always occur because of the existence of competing reactions. Point these out.

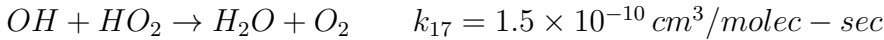
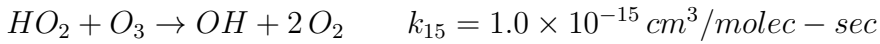
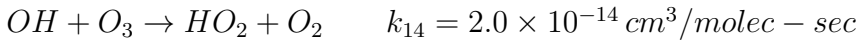
3. Specify two ways in which the presence of NO_y species slows down ozone destruction from ClO .

4. Give two ways in which the presence of NO_x ($= NO + NO_2$) slows down rates of ozone destruction due to other catalytic cycles (either HO_x or ClO_x). In your discussion specify the relevant reactions.

6. (i) Write down a complete sequence of reactions by which members of the NO_y family destroy HO_x . By complete sequence is meant a cycle in which each NO_y species involved gets produced and destroyed.

(ii) Write down a complete sequence of reactions by which members of the NO_y family can produce HO_x .

7. Consider the following reactions only:



$$[M] = 2 \times 10^{18} \text{ molec}/\text{cm}^3.$$

$$\text{OH} = 0.6 \text{ pptv}$$

$$\text{O}_3 = 4 \text{ ppmv}$$

(i) HO_x destroys O_x in the stratosphere via a catalytic cycle. What is the sequence of reactions in this cycle?

(ii) Estimate the length of time it takes a HO_x molecule to destroy one O_x .

(iii) Estimate the number of O_x molecules destroyed by one HO_x before it itself is destroyed. (ie. the HO_x chain length).

8. How does the presence of NO_x (NO or NO_2) inhibit O_x destruction by HO_x ? Specify relevant reaction(s).

9. How does the presence of HO_x (OH or HO_2) inhibit O_x destruction by NO_x ? Specify relevant reaction(s).

11. How does O_x destruction by ClO_x depend on NO_x ? Give a reason for this dependence. Specify a reaction if possible.

12. (i) Write down a sequence of reactions involving HO_x or NO_x species which results in catalytic ozone (O_3) destruction.

(ii) How would you express the rate of O_x destruction by this cycle?

13. Write out two catalytic cycles which destroy O_x in the stratosphere.

14. In the stratosphere, O_x is destroyed by catalytic cycles involving HO_x , NO_x , and ClO_x radicals. For each family below, indicate if the N_2O_5 aerosol reaction increases or decreases O_x destruction by that family, and give a reason why.

(i) HO_x

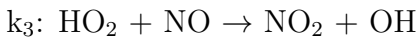
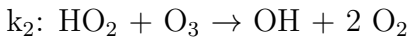
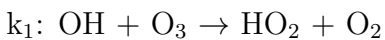
(ii) NO_x

(iii) ClO_x

15. Show that the net rate of O_x destruction by HO_x can be written:

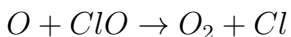
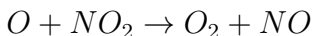
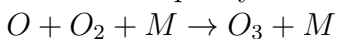
$$d[\text{O}_x]/dt = -2k_2[\text{HO}_2][\text{O}_3],$$

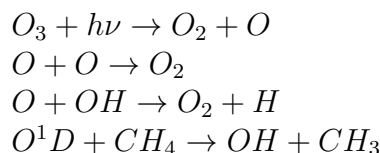
where one assumes that HO_x interacts with O_x through the following reactions:



Hint: By far the dominant sink of NO_2 is: $\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}$.

16. Define the O_x family. Why is the lifetime of O_x much longer than the lifetimes of its individual members? Specify which of the following reactions destroy, produce, or conserve O_x .





17. Studies have shown that NO_x injected into the stratosphere from high speed aircraft will probably decrease the rate of ozone destruction by ClO_x . Why? Specify a relevant reaction in your answer.

18. The rate of ozone destruction due to NO_x ($NO + NO_2$) is usually defined as $-2k[O][NO_2]$, where k is the reaction constant for the $O + NO_2$ reaction. This is based on the assumption that NO will *always* react with O_3 to make NO_2 . This is incorrect.

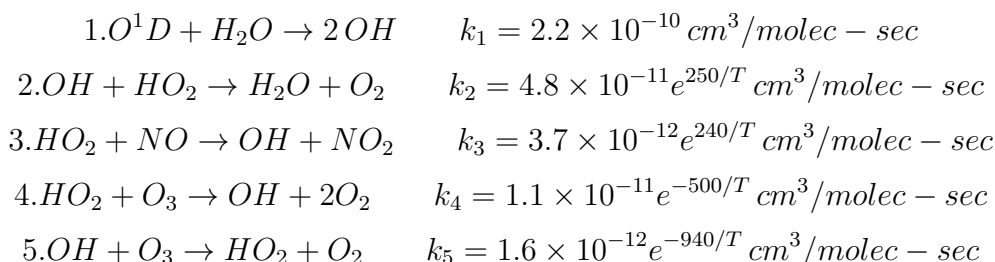
(i) What is the next most important NO to NO_2 conversion pathway? (Do this by looking in JPL 94 for things that give up an oxygen atom to NO , and calculate the NO lifetime for this reaction based on the JPL concentrations.)

(ii) What is the probability that they will occur relative to the likelihood of NO reacting with ozone? Use concentrations and temperatures at 20 km of JPL '94.

(iii) If these alternative pathways are taken, will ozone still be destroyed ordinarily? Are you in danger of "double counting"? ie., counting one net ozone destruction twice from two different cycles?

Stratospheric Ozone: HOx Partitioning (S3)

2. Consider the following reactions only:



(i) The pressure is 50 hPa, the temperature is 220 K, $O_3 = 3$ ppmv, $H_2O = 5$ ppmv, $NO = 100$ pptv, and $[O^1D] = 3$ molec/cm³. Using appropriate "family-style" approximations, solve for the concentration of OH . (If I asked this equation again I would break it into parts, and give you the values of the reaction constants. The OH/HO_2 ratio can be solved from using reactions 3, 4, 5 only. Then impose steady state on HO_x . Reaction 1 produces HO_x , and reaction 2 destroys HO_x .)

(ii) What is the lifetime of water with respect to attack by O^1D ?

4. What is a reaction which destroys HO_x in the stratosphere?

5. (i) Derive a steady state expression for the concentration of H_2O_2 in terms of the concentrations of $[OH]$, $[HO_2]$, $J_{H_2O_2}$, and relevant reaction rates.

(ii) Use this expression and the JPL concentration profiles to predict the H_2O_2 concentration at 20 km and compare your answer with the JPL modeled concentration at 20 km.

7. (i) Derive a steady state expression for the concentration of H_2O_2 in terms of the concentrations of $[OH]$, $[HO_2]$, $J_{H_2O_2}$, and relevant reaction rates.

(ii) Use this expression and the JPL concentration profiles to predict the H_2O_2 concentration at 20 km and compare your answer with the JPL modeled concentration at 20 km.

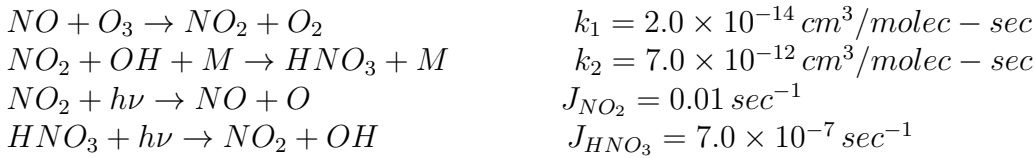
8. (i) Define f as the fraction of O^1D atoms that react with water vapor to make two OH hydroxyl radicals rather than than being quenched back to O . Calculate this at the ground with a temperature

of 300 K and 100 percent humidity, and at 30 km with a temperature consistent with the JPL profile and 5 ppmv (parts per million) of water vapor.

(ii) What is the O_x lifetime associated with $O^1D + H_2O$ at the two heights? For 30 km, assume the $J_{O_3 \rightarrow O^1D}$ value in JPL, and for the ground, extrapolate from 10 km.

Stratospheric Ozone: NOx Partitioning (S4)

9. Assume the following reactions:



The pressure ($[M]$) dependence has been included in k_2 .

The mixing ratio of O_3 is 2 ppmv.

The mixing ratio of OH is 1.0 pptv.

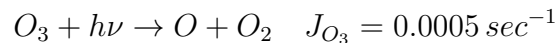
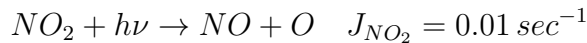
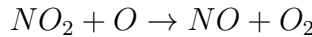
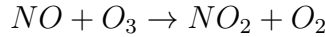
Assume that NO_x ($= NO + NO_2$) can be treated as a family.

$$[M] = 2 \times 10^{18} \text{ molec/cm}^3.$$

(i) Evaluate the $[NO]/[NO_2]$ ratio. You may use family style and steady state approximations.

(ii) Evaluate the $[NO_x]/[HNO_3]$ ratio. You may use family style and steady state approximations.

10. Assume the following set of reactions:



The mixing ratio of O_3 is 5 ppmv.

$$[M] = 2 \times 10^{18} \text{ molec/cm}^3.$$

The mixing ratio of NO_x ($= NO + NO_2$) is 500 pptv.

The temperature is 220 K.

Using family style and steady state approximations,

(i) What is the concentration of atomic oxygen?

(ii) What is the NO/NO_2 ratio?

(iii) What is the lifetime of NO_2 with respect to photolysis?

(iv) What is the lifetime of NO_2 with respect to reaction with O?

(v) The rate of O_x destruction from NO_x is often written $-2k[NO_2][O]$. Explain.

(vi) What is the lifetime of O_x with respect to destruction by NO_x ?

11. For simplicity, let $[NO_y] = [NO] + [NO_2] + [HNO_3]$.

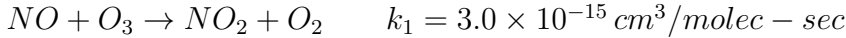
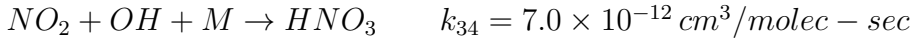
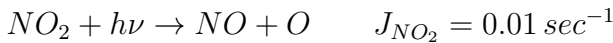
$$[NO_x] = [NO] + [NO_2]$$

$$[M] = 2 \times 10^{18} \text{ molec/cm}^3.$$

$$\text{OH} = 0.6 \text{ pptv}$$

$$\text{O}_3 = 4 \text{ ppmv}$$

Consider the following reactions only:



(i) Estimate the $[\text{NO}]/[\text{NO}_2]$ ratio using family style approximations for NO_x .

(ii) Assuming that NO_x is in steady state, and using the $[\text{NO}]/[\text{NO}_2]$ ratio given above, solve for the $[\text{NO}_x]/[\text{HNO}_3]$ ratio.

(iii) What is the lifetime of NO_x with respect to conversion to HNO_3 ?

12. Assume the following reactions:



The pressure ($[M]$) dependence has been included in k_2 (i.e. leave out $[M]$ when writing out this reaction rate.)

The mixing ratio of O_3 is 2 ppmv.

The mixing ratio of OH is 1.0 pptv.

Assume that NO_x ($= \text{NO} + \text{NO}_2$) can be treated as a family.

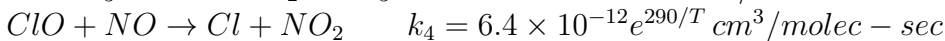
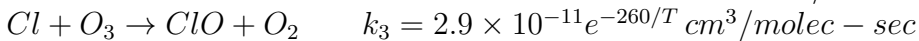
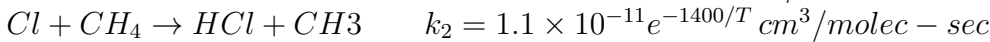
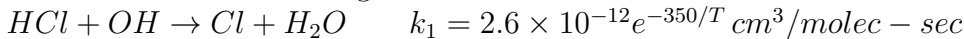
Total molecular density: $[M] = 2 \times 10^{18} \text{ molec/cm}^3$.

(i) Evaluate the $[\text{NO}]/[\text{NO}_2]$ ratio. You may use family style and steady state approximations.

(ii) Evaluate the $[\text{NO}_x]/[\text{HNO}_3]$ ratio. You may use family style and steady state approximations.

Stratospheric Ozone: ClO_x Partitioning (S5)

16. Consider the following reactions.



Assume:

Temperature = 220 K

Pressure = 50 hPa

$\text{O}_3 = 2 \text{ ppmv}$

$\text{CH}_4 = 1.6 \text{ ppmv}$

$\text{OH} = 1 \text{ pptv}$

$\text{NO} = 500 \text{ pptv}$

(i) Use local steady state assumptions to derive an expression for the $\frac{\text{Cl}}{\text{HCl}}$ ratio.

(ii) Treat ClO_x ($= \text{Cl} + \text{ClO}$) as a subfamily of Cl_y , and use local steady state, to derive and expression for the $\frac{\text{Cl}}{\text{ClO}}$ ratio.

(iii) Use these expressions and the above species concentrations to calculate the $\frac{\text{ClO}}{\text{HCl}}$ ratio.

17. This question involves estimating the increase in ClO associated with a decrease in NO_x, as might occur for example from a volcanic eruption. *This is a hard question. If gave in the future would break up into smaller parts.*

Assume:

NO_x decreases from 400 pptv to 200 pptv.

The effect of ClO on NO_x partitioning is negligible.

Consider the species Cl, ClO, ClONO₂, HCl, NO, NO₂, CH₄, OH, and O₃ only.

All species can be assumed to in steady state, or specified as given below.

$$[Cl_y] = [ClO] + [Cl] + [ClONO_2] + [HCl]$$

Total Cl_y is 2 ppbv.

NO_x (= NO + NO₂) and ClO_x (= Cl + ClO) can be treated as families.

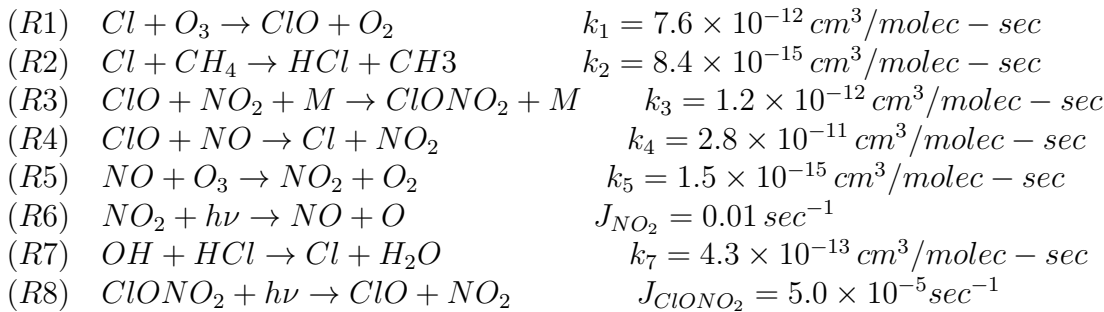
$$[OH] = 1 \text{ pptv (independent of NO}_x\text{)}$$

$$[O_3] = 2 \text{ ppbv}$$

$$[CH_4] = 1.0 \text{ ppmv}$$

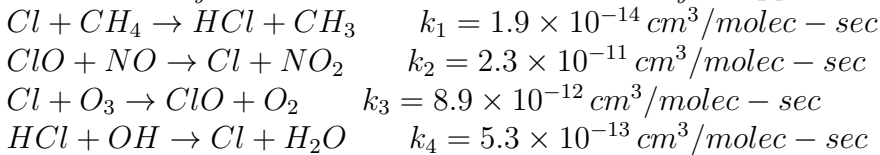
$$\text{Temperature} = 195 \text{ K, Pressure} = 50 \text{ hPa, } [M] = 1.8 \times 10^{18} \text{ molec/cm}^3.$$

Assume the following reaction set:



- (i) Derive an expression for the ClO/ClONO₂ ratio.
- (ii) Derive an expression for the Cl/HCl ratio.
- (iii) Derive an expression for the Cl/ClO ratio.
- (iv) Evaluate the mixing ratio of ClO when NO_x = 400 pptv.
- (v) Evaluate the mixing ratio of ClO when NO_x = 200 pptv.

18. Define Cl_y = Cl + ClO + HCl. The total Cl_y is 2 ppbv. Assume the following reactions:



You may treat ClO_x (= Cl + ClO) as a family.

You can assume that HCl is in steady state with ClO_x.

NO : 100 pptv

O₃ : 2 ppmv

CH₄ : 1.2 ppmv

OH : 1 pptv

- (i) Evaluate the Cl/ClO ratio.
- (ii) Evaluate the Cl/HCl ratio.
- (iii) Evaluate the ClO mixing ratio (in pptv)

- 3.** It has been reasonably well established from aircraft measurements that denitrification occurs in both the Arctic and Antarctic. What measurements have been used to establish this? Summarize the arguments based on these measurements used to support denitrification. A schematic plot may help.
- 4.** As an air parcel is transported within the Brewer-Dobson circulation, would you expect the mixing ratio of NO_y ($= \text{NO} + \text{NO}_2 + \text{HNO}_3 + \text{NO}_3 + \text{N}_2\text{O}_5 + \text{ClONO}_2$) to increase or decrease with time? What is the main reason for this? (*Increases with time due to O1D attack on N2O*).
- 5.** During the Antarctic winter, it is believed that nitric acid trihydrate particles (NAT or type I PSC's) serve as nucleation sites for type II PSC's consisting of ice. Type II PSC's are large enough to fall significant distances during their lifetime. The resulting depletion of NO_y within the Antarctic polar vortex is called *denitrification*. It is thought that this enhances ozone depletion by slowing down the conversion of active chlorine ($\text{Cl} + \text{ClO} + \text{Cl}_2\text{O}_2$ etc.) to reservoir chlorine ($\text{HCl} + \text{ClONO}_2$). How would it do this?
- 6.** (i) What is denitrification?
(ii) How does it enhance polar ozone depletion?
(iii) Ozone depletion does not occur inside the polar night. Why?
(iv) In the absence of denitrification NO_y mixing ratios will be typically higher inside the vortex than outside. Why?
- 8.** The only sink of NO_y in the stratosphere (other than the fallout of nitrogen containing polar stratospheric cloud crystals over the winter poles) is the $\text{N} + \text{NO} \rightarrow \text{N}_2 + \text{O}$ reaction. Calculate the lifetime of NO_y associated with this reaction at 30 km using the JPL 1994 profiles.
- 9.** Figure 19.8 shows simultaneous measurements of NO_y and N_2O taken at about 20 km from the ER-2. The decrease in N_2O is at 76° N, and the increase in NO_y at the same latitude, are associated with a crossing of the polar vortex. (*This would be an interesting assignment question but would not be given on a quiz.*)
(i) Make a scatter plot of NO_y versus N_2O (ie. NO_y against N_2O).
(ii) Use the plot to estimate the fraction of N_2O molecules that undergo reaction with O^1D to produce 2 NO.

Stratospheric Ozone: Aerosol Chemistry (S7)

- 11.** Studies have shown that the injection of NO_x into the stratosphere from a projected fleet of high flying aircraft will decrease chlorine catalyzed ozone destruction. Explain.
- 12.** The effect on ozone levels of a volcanic eruption which increases aerosol surface areas in the stratosphere depends on the chemical composition of the stratosphere. Explain.
- 13.** It is currently accepted that the increases in aerosol surface area in the stratosphere associated with explosive volcanic eruptions reduce total column ozone. But one hundred years ago, it is likely that these reductions were smaller, or that a volcanic eruption may have actually increased total column ozone. Give an argument as to why the response of the ozone layer to volcanic eruptions is likely to have changed in this way.
- 15.** For each of the following radical families, indicate whether the N_2O_5 aerosol reaction increases or decreases ozone destruction by that family. Also give a reason for this change, being as specific as possible with a particular reaction(s) in your explanation.
(i) NO_x

- (ii) HO_x
- (i) ClO_x

20. It has been recognized that extremely large volcanic eruptions such as the eruption of Mt. Pinatubo will not reduce NO_x/NO_y ratios to zero in the stratosphere even though they dramatically increase sulphate aerosol surface areas. At some point, NO_x/NO_y ratios become insensitive to increases in aerosol surface area. This is referred to as saturation. Aerosol mediated NO_x to HNO₃ conversion occurs at night when NO₂ is converted to NO₃, then N₂O₅, and the N₂O₅ then reacts with water on the aerosol. When there is lots of aerosol surface area, virtually every N₂O₅ created at night gets converted to HNO₃ rather than being photolyzed to NO_x the next morning. In this case, the rate limiting step in converting NO_x to HNO₃ via the aerosol pathway becomes the formation of NO₃. An estimate of the upper limit effect of the the N₂O₅ aerosol reaction can be obtained by assuming that every NO₃ formation reaction at night effectively destroys two NO_x. *This question is too hard to ask in a quiz*

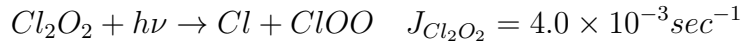
- (i) Why two NO_x?
- (ii) Calculate the diurnally averaged (24 hour averaged) NO_x lifetime associated with the aerosol loss. Assume a 12 hour night and the temperature, ozone concentration, and number densities at 20 km in JPL '97. (Hint: the NO₂ concentration at night = the NO_x concentration.)
- (iii) Make an estimate of the diurnally averaged NO_x lifetime associated with the NO₂ + OH reaction. As a rule of thumb, it is fairly accurate to say that the diurnally averaged concentration of a radical like OH is about one-third the noon value, given a 12 hour day. Also you will need for this question to express the noon NO₂ concentration in terms of NO_x, using the usual steady state approximations. You can assume that NO_x is constant over the day.
- (iii) What is the net lifetime of NO_x with respect to both loss processes. (Hint: you add lifetimes as reciprocals. Eg. the net loss lifetime from two processes is

$$\frac{1}{\tau_{net}} = \frac{1}{\tau_1} + \frac{1}{\tau_2}.$$

- (iv) What is the diurnally averaged nitric acid photolysis rate (the J value) at 20 km? Again divide noon value by three to get the diurnally averaged rate.
- (v) Estimate the NO_x/NO_y ratio with and without the N₂O₅ aerosol reaction. Assume that the contributions of NO₃, N₂O₅, and ClONO₂ to NO_y are small enough to be ignored. There are a couple of different ways of doing this. One is to start from as assumption of NO_x steady state, using the approximations for the NO_x and HNO₃ loss rates given above, or proceed directly from the relative lifetimes.

Stratospheric Ozone: Polar Stratospheric Clouds (S8)

21. (i) Suppose that reactions on polar stratospheric clouds (PSC's) have converted most of the reservoir chlorine species (HCl and ClONO₂) to active chlorine ClO_x, where ClO_x is defined as the sum of ClO and 2.*Cl₂O₂. If the mixing ratio of ClO_x is 2 ppbv, estimate the mixing ratio of ClO. Assume that the partitioning of ClO_x can be calculated assuming photochemical equilibrium, that the reactions which determine this partitioning are given below, and that the photolysis of Cl₂O₂ is effectively the source of two ClO since ClOO rapidly decomposes to Cl and Cl reacts rapidly with ozone to make ClO. The pressure is 60 hPa (about 20 km) and the temperature is 195 K.

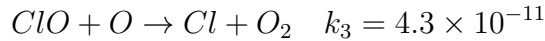
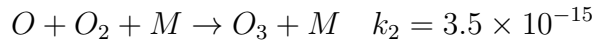
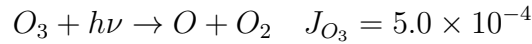


The density [M] can be calculated from temperature T and pressure P (in hPa) using

$$[M] = \frac{P}{T \cdot 1.38 \times 10^{-19}}$$

(ii) The rate of ozone destruction by the cycle involving the chlorine dimer Cl_2O_2 is $2k_1[ClO][ClO]$. What is the lifetime of ozone with respect to this cycle if the ozone mixing ratio is 3 ppmv?

(iii) Calculate the lifetime of ozone with respect to the $ClO + O$ catalytic cycle. Assume that O and O^1D form a very small fraction of O_x , and that the O_x family can be partitioned using photochemical equilibrium assumptions.



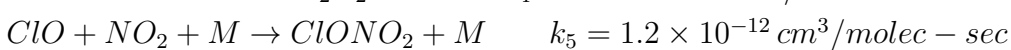
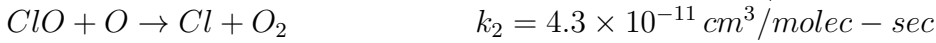
23. (i) Write down two reactions that occur on the surfaces of polar stratospheric clouds (PSC's).

(ii) What is their effect on nitrogen and chlorine partitioning?

(iii) Why do they increase ozone destruction?

24. Write down a reaction that occurs on polar stratospheric clouds and explain why it leads to enhanced ozone destruction.

25. Consider the following reactions involving Cl, ClO, Cl_2O_2 , HCl, ClONO₂, O₃, O, NO, and NO₂. (Note: the products of Cl_2O_2 photolysis are taken to be Cl + Cl + O₂; ie. the ClOO produced by Cl_2O_2 photolysis is assumed to immediately thermally dissociate into Cl and O₂.) (*On a quiz, this question would be broken into smaller parts to be more easily solvable.*)



Also assume:

Temperature = 195 K

Pressure = 50 hPa

$[M] = \frac{P \times 7.25 \times 10^{18}}{T}$ molec/cm³, P in hPa and T in K

O₃ = 2 ppmv

CH₄ = 1.6 ppmv

NO = 50 pptv

ClO = 1500 pptv

Note: the [M] dependence of the three body rate constants has already been absorbed into the rate constant.

(i) Write down two catalytic cycles involving ClO which destroy ozone.

(ii) Calculate the rate of ozone destruction from each of the two cycles. Convert your answers to ppbv per day. You may use family style approximations to partition O_x .

(iii) What is the lifetime of O_3 with respect to each of the two cycles?

(iv) Calculate the Cl_2O_2 mixing ratio (in pptv). You may assume that Cl_2O_2 is in steady state.

(v) Calculate the mixing ratio of Cl (in pptv). You may assume that ClO_x (= Cl + ClO + Cl_2O_2) can be treated as a family and partitioned in the usual way.

(vi) Calculate the lifetime of ClO_x with respect to conversion to HCl.

(vii) Calculate the lifetime of ClO_x with respect to conversion to $ClONO_2$. You may also use family style approximations to partition NO_x (= NO + NO_2).

26. After an air parcel has been exposed to a PSC, how does the presence of NO_x in the air parcel increase the rate at which ClO_x is converted back to both $ClONO_2$ and HCl? Be as specific as possible in referring to the particular reactions, or reaction sequences, by which this occurs.

27. Number the following events as they would occur in sequence over the South Pole during a polar ozone depletion event. (i.e. 1 - 6 with 1 the first event that occurs.)

Cl_2 photolyzes

NO_x increases

PSC's start to form

Polar vortex temperatures become colder

Ozone and ClO_x become anticorrelated

HCl mixing ratios decrease

28. A plane flying in the stratosphere is equipped to measure ClO, O_3 , and NO. These measurements give:

[NO] = 20 pptv (parts per trillion)

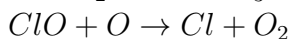
[O_3] = 6 ppmv (parts per million)

[ClO] = 2000 pptv (parts per trillion)

Assume the following reactions:



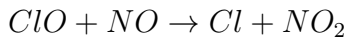
$$k_1 = 1.7 \times 10^{-15} \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$$



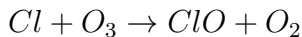
$$k_2 = 4.3 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$$



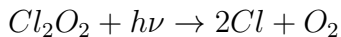
$$k_3 = 6.4 \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$$



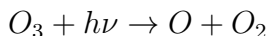
$$k_4 = 2.8 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$$



$$k_5 = 7.6 \times 10^{-12} \text{ cm}^3 / \text{molec} - \text{sec}$$



$$J_{Cl_2O_2} = 1.0 \times 10^{-3} \text{ sec}^{-1}$$



$$J_{O_3} = 6 \times 10^{-4} \text{ sec}^{-1}$$

The temperature is $T = 195$ K.

The total number density of the air is $[M] = 2 \times 10^{18}$ molec/cm³.

You may treat the pressure dependent reaction rates as if the $[M]$ dependence is included in the k 's.

Use all family partitioning and steady state approximations you think appropriate.

$$[\text{ClO}_x] = [\text{Cl}] + [\text{ClO}] + [\text{Cl}_2\text{O}_2]$$

$$[\text{O}_x] = [\text{O}] + [\text{O}_3]$$

$$[\text{O}_2] = 0.2 [\text{M}]$$

- (i) Calculate the $[\text{O}]/[\text{O}_3]$ ratio.
- (ii) Calculate the lifetime of O_x with respect to destruction by the $\text{ClO} + \text{O}$ catalytic cycle.
- (iii) Calculate the mixing ratio of Cl_2O_2 .
- (iv) Calculate the lifetime of O_x with respect to destruction by the $\text{ClO} + \text{ClO}$ reaction catalytic cycle.
- (v) Estimate the Cl/ClO ratio.

29. What is wrong with this sentence: "The annual springtime 50 % reduction in total ozone column over the Antarctic has always occurred because polar stratospheric clouds have always existed at this time in the Antarctic."

30. Provided there is sufficient total reactive chlorine Cl_y , what are the two *main* preconditions for rapid polar ozone destruction?

31. The ClO mixing ratio of an air parcel is measured to be 2 ppbv.

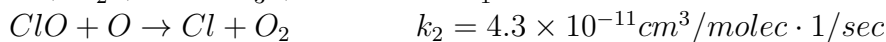
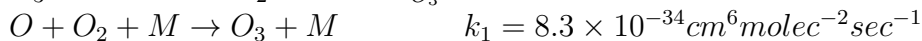
The temperature is $T = 195 \text{ K}$.

The mixing ratio of O_3 is 6 ppmv.

The total number density of the air is $[\text{M}] = 2 \times 10^{18} \text{ molec/cm}^3$.

$$[\text{O}_2] = 0.2 [\text{M}]$$

Consider the following reactions only:



Using appropriate family style and steady state approximations:

- (i) What is the lifetime of O_x with respect to destruction the $\text{O} + \text{ClO}$ cycle?
- (ii) What is the lifetime of O_x with respect to destruction the $\text{ClO} + \text{ClO}$ dimer cycle?
- (iii) Roughly plot how the rates of ozone destruction from the two O_x destroying cycles given above would depend on the ClO concentration.

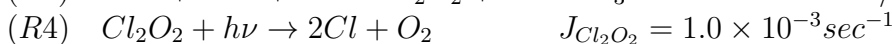
34. We have discussed in class three catalytic cycles involving chlorine which destroy ozone. In the reaction labeling given below, one of these is reaction 1 followed by reaction 2, and another is reaction 3, followed by reactions 4 and 1. Until we started discussing ozone depletion chemistry, we ignored the second cycle. This question involves justifying that the dimer cycle can be ignored in the background case. Let $[\text{ClO}] = 50 \text{ pptv}$ in the background case, and $[\text{ClO}] = 2000 \text{ pptv}$ in an air mass perturbed by PSC's. In answering this question, make any approximations you think can be justified, eg. family partitioning etc. Unless otherwise specified, all species can be assumed to be in steady state. Consider the reactions listed below only.

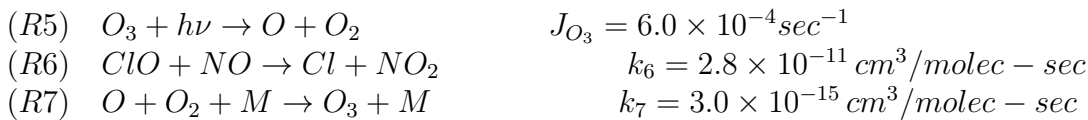
$$[\text{ClO}_x] = \text{Cl} + \text{ClO} + 2 \text{ Cl}_2\text{O}_2$$

$$[\text{O}_3] = 2 \text{ ppmv}$$

$$[\text{NO}] = 100 \text{ pptv}$$

Temperature = 195 K, Pressure = 50 hPa, $[\text{M}] = 1.8 \times 10^{18} \text{ molec/cm}^3$.





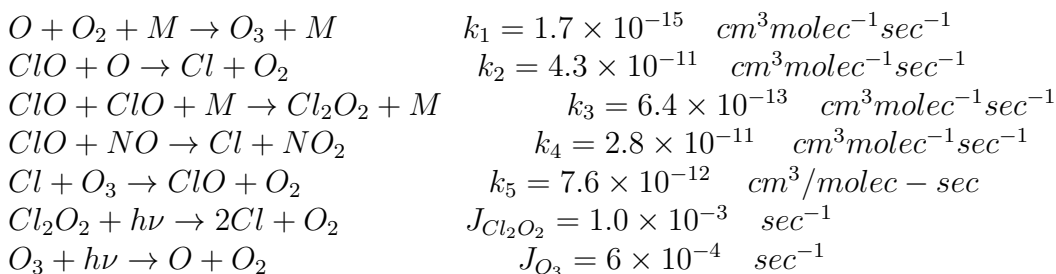
- (i) Calculate the mixing ratio (in pptv) of Cl₂O₂ in the background case.
- (ii) Calculate the mixing ratio (in pptv) of Cl₂O₂ in the PSC perturbed case.
- (iii) Calculate the mixing ratio (in pptv) of O.
- (iv) What percent of the chlorine ozone destruction in the background case is due to the dimer cycle?
- (v) What percent of the total ozone destruction in the PSC perturbed case is due to the dimer cycle?

35. What is the main reason polar ozone depletion is more extensive over the South Pole than the North Pole?

41. A plane flying in the stratosphere is equipped to measure ClO, O₃, and NO. These measurements give the following mixing ratios:

$$\begin{array}{l}
C_{NO} = 20 \text{ pptv (parts per trillion)} \\
C_{O_3} = 6 \text{ ppmv (parts per million)} \\
C_{ClO} = 2000 \text{ pptv (parts per trillion)}
\end{array}$$

Assume the following reactions:



The temperature is T = 195 K.

The total number density of the air is [M] = 2 × 10¹⁸ molec/cm³.

You may treat the pressure dependent reaction rates as if the [M] dependence is included in the k's.

Use all family partitioning and steady state approximations you think appropriate.

$$\begin{array}{l}
[ClO_x] = [Cl] + [ClO] + [Cl_2O_2] \\
[O_x] = [O] + [O_3] \quad [O_2] = 0.2 [M]
\end{array}$$

- (i) Calculate the [O]/[O₃] ratio.
- (ii) Calculate the lifetime of O_x with respect to destruction by the ClO + O catalytic cycle.
- (iii) Calculate the mixing ratio of Cl₂O₂.
- (iv) Calculate the lifetime of O_x with respect to destruction by the ClO + ClO reaction catalytic cycle.
- (v) Estimate the Cl/ClO ratio.

Stratospheric Ozone: Ozone variability (S9)

44. Ozone column amounts tend to be higher in mid-latitude and polar regions than in the tropics even though ozone production rates are higher in the tropics. Explain

45. In which regions of the stratosphere is the concentration of ozone least likely to be in instantaneous photochemical equilibrium with its sources and sinks? Where is equilibrium most likely to be valid?
46. Ozone columns and UV exposure fluctuate from day to day in response to weather systems which change the height of the tropopause. Why?
47. Plot how the total ozone column depends on season (from January through December) at a typical mid-latitude location.
48. Stratospheric ozone production rates are largest in the tropics but ozone column amounts are higher in mid-latitudes. Why?
49. Plot the typical variation of ozone column amounts (Dobson units) over a year at a Northern Hemisphere mid-latitude location. What is the main reason for this variation?
50. Plot how the ozone column varies over the course of a year at a mid-latitude location. What is the main reason for this variation?
51. (i) Plot how tropopause height typically depends on season at a typical mid-latitude location in going from January to December.
(ii) Plot how ozone column typically depends on season at a typical mid-latitude location in going from January to December.
(iii) On a clear day, what are the two main variables that affect the level of UV radiation at the surface?
(iv) What time of year would you typically expect UV levels at the surface to be maximized at a typical mid-latitude location? Be as specific as possible. (2 point)

Stratospheric Ozone: CFC's and other long-lived tracers (S10)

52. An air parcel enters the stratosphere from the troposphere with particular mixing ratios of CH₄ (methane), N₂O, NO_y, CFC-11, and water. Which of these gases will see their mixing ratios increase, which will decrease, and which will be unchanged?
53. (i) What is the main natural "source gas" of Cl_y to the stratosphere? (0.5 point)
(ii) What is the main natural "source gas" of HO_x to the stratosphere? (0.5 point)
(iii) What is the main natural "source gas" of NO_y to the stratosphere? (0.5 point)
54. Most of the CFC's released into the atmosphere are ultimately destroyed (and release their chlorine atoms) in the tropical stratosphere, where levels of UV light are high. It is sometimes claimed that if CFC's were destroying ozone, we would therefore be more likely to observe ozone destruction in the tropics, and not in the polar regions as actually happens. Why is this reasoning incorrect?
55. Why are the CFC's chemically stable in the troposphere but not in the stratosphere?
56. Suppose the water vapor concentration in the stratosphere were to double. Discuss two ways how this might lead to increased ozone destruction in the stratosphere. (*More HO_x and more PSC's.*)

For the most part, the only way to get analytic approximations for relationships between species concentrations is to use family style approximations in conjunction with local steady state assumptions. Try to be familiar with this approach and how it can be applied in different situations. The most difficult thing to understand about it is why it is possible to ignore a reaction in one case but

not another. For example, why can I ignore O_2 photolysis when calculating the O/O_3 ratio, but not when calculating the O_x concentration?

Chapter 11: Oxidizing Power of the Troposphere (X11)

Oxidizing Power of the Troposphere: HO_x Production (T1)

1. Why is the hydroxyl radical sometimes referred to as the “detergent” of the atmosphere. Give two factors which affect its concentration.
2. What are the two main variables which drive the seasonal variation of OH concentrations in the troposphere?
3. (i) Where in the troposphere is the concentration of OH typically largest?
(ii) Give two reasons for this.
4. The input of NO_x and CO into the troposphere is many times larger now than it was one hundred years ago. The oxidation of each of these species (to HNO_3 and CO_2 respectively) results in the loss of one OH. But the concentration of OH has probably remained stable, or in some areas increased, over the past one hundred years. What is the main reason why OH has not gone down as much as you might expect?
5. (i) How is HO_x produced?
(ii) What are two factors that affect the production of HO_x ?

6. Assume the following conditions in the upper troposphere: (*This question would be simplified if given on a quiz.*)

$$T = 220 \text{ K}$$

$$\text{Pressure} = 200 \text{ hPa}$$

$$P_{H_2O} = 0.05 \text{ hPa}$$

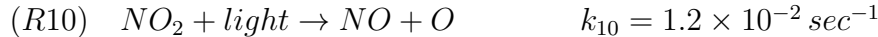
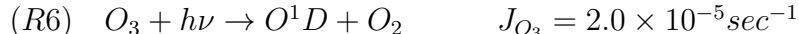
$$[M] = 6.6 \times 10^{18} \text{ molec/cm}^3$$

$$C_{NO} = 50 \text{ pptv}$$

$$C_{CO} = 80 \text{ ppbv}$$

$$[O_3] = 40 \text{ ppbv}$$

Assume the following reaction set:



Assume HO_x , NO_x , and $[O^1D]$ are in steady state, and that HO_x and NO_x can be partitioned using family style approximations.

- (i) Solve for $[OH]/[HO_2]$.

- (ii) Solve for $[\text{NO}]/[\text{NO}_2]$. (Assume HO2 small.)
- (iii) Solve for $[\text{O}^1\text{D}]$ (molec/cm³).
- (iv) Calculate the ozone production efficiency of NO.
- (v) Solve for the HO₂ mixing ratio (in pptv). (Hint: The solution involves solving a quadratic equation. Explain how you would solve if you don't have time for the answer. $Ax^2 + Bx + C = 0$ and $x = \frac{-B \pm \sqrt{B^2 - 4AC}}{2A}$)

(i) *Answer* To solve for OH/HO2, restrict attention to HOx partitioning reactions: 2,7,3,1.

$$\text{POH} = \text{LOH}$$

$$k_3[\text{JO}_2][\text{O}_3] + k_1[\text{HO}_2][\text{NO}] = k_2[\text{OH}][\text{O}_3] + k_7[\text{OH}][\text{CO}]$$

Re-arranging gives:

$$[\text{OH}]/[\text{HO}_2] = (k_3[\text{O}_3] + k_1[\text{NO}]) / (k_2[\text{O}_3] + k_7[\text{CO}])$$

$$[\text{O}_3] = \text{CO}_3[\text{M}], \text{ etc.}$$

Since [M] is on the top and bottom for all species,

$$[\text{OH}]/[\text{HO}_2] = (k_3 \cdot \text{CO}_3 + k_1 \cdot \text{CNO}) / (k_2 \cdot \text{CO}_3 + k_7 \cdot \text{CCO})$$

$$\text{CO}_3 = 40\text{E-}09, \text{ CNO} = 50\text{E-}12, \text{ CCO} = 80\text{E-}09$$

You should know what ppmv, ppbv, pptv are etc. It also very important to know that it is concentration (not mixing ratios) that enter the equation, though as in the case above, [M] can cancel.

$$[\text{OH}]/[\text{HO}_2] = 0.041$$

(ii) *Answer* NOx is a family, so only relevant reactions are k1,k10,k11, but since you don't know [HO2] I said you could ignore (in reality it is usually small compared to NO+O3).

$$k_{10}[\text{NO}_2] = k_{11}[\text{NO}][\text{O}_3]$$

$$[\text{NO}]/[\text{NO}_2] = k_{10}/(k_{11}[\text{O}_3]) = 13.4$$

(iii) *Answer*

$$\text{JO}_3[\text{O}_3] = k_5[\text{O}^1\text{D}][\text{N}_2] + k_4[\text{O}^1\text{D}][\text{H}_2\text{O}]$$

Since [M] would be on both sides, can write:

$$\text{JO}_3 \cdot \text{CO}_3 = k_5[\text{O}^1\text{D}] \cdot \text{CN}_2 + k_4[\text{O}^1\text{D}] \cdot \text{CH}_2\text{O}$$

$$[\text{O}^1\text{D}] = \text{JO}_3 \cdot \text{CO}_3 / (k_5 \cdot \text{CN}_2 + k_4 \cdot \text{CH}_2\text{O})$$

$$\text{CN}_2 = 0.8$$

$$\text{CH}_2\text{O} = 0.05/200$$

$$\text{CO}_3 = 40\text{E-}09$$

$$\text{This gives } [\text{O}^1\text{D}] = 0.03 \text{ molec/cm}^3$$

(iv) *Answer*

$$e = \text{PO}_3/\text{LNO}_x = k_1[\text{NO}][\text{HO}_2]/k_9[\text{NO}_2][\text{OH}]$$

Using the ratios $[\text{NO}]/[\text{NO}_2]$ and $[\text{HO}_2]/[\text{OH}]$ above, get $e = 300$

(v) *Answer* Set LHOx = PHOx

$$k_8[\text{HO}_2][\text{HO}_2] + k_9[\text{OH}][\text{NO}_2] = 2 \cdot k_4[\text{O}^1\text{D}][\text{H}_2\text{O}]$$

Computationally, it saves time to replace all concentrations with mixing ratios. Can do this since there is an [M][M] in each term.

$$k_8 \cdot \text{CHO}_2 \cdot \text{CHO}_2 + k_9 \cdot \text{COH} \cdot \text{CNO}_2 = 2 \cdot k_4 \cdot \text{CO}^1\text{D} \cdot \text{CH}_2\text{O}$$

Above found [O¹D], so know CO¹D = [O¹D]/[M].

Also know CH₂O.

Use $R = [\text{OH}]/[\text{HO}_2]$ from above, and given CNO₂.

$$\text{CHO}_2 \cdot \text{CHO}_2 + (k_9/k_8) \cdot R \cdot \text{CHO}_2 \cdot \text{CNO}_2 - 2 \cdot k_4/k_8 \cdot \text{CO}^1\text{D} \cdot \text{CH}_2\text{O} = 0$$

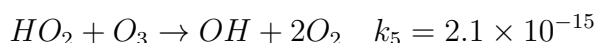
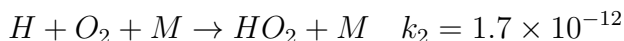
This is a quadratic equation in CHO₂, with A = 1.

Should get $\text{CHO}_2 = 16$ pptv.

7. There has been some speculation on how ozone depletion in the stratosphere might affect the oxidizing capacity of the troposphere. Discuss two mechanisms of how this might occur.
8. Ozone columns have decreased over the past several decades. How might this have affected concentrations of OH in the troposphere? Specify a relevant reaction if possible.
9. (i) Plot the typical dependence of the OH concentration on NO in the troposphere.
(ii) What is the main reason for the dependence of OH on NO at low NO?
(iii) What is the main reason for the dependence of OH on NO at high NO?
(iv) Give three species for which OH attack is the main oxidation mechanism.
(v) How is OH thought to have changed over North America since preindustrial times?
(vi) What is the main reason for this change?
(vii) Is this change mainly good or bad? Explain.
10. (i) Is the concentration of OH in remote regions of the Southern Hemisphere likely to have increased or decreased since preindustrial times. Explain.
(ii) Is the average concentration of OH near the surface over land in the Northern Hemisphere likely to have increased or decreased since preindustrial times. Explain.
11. (i) Define f as the fraction of O^1D atoms that react with water vapor to make two OH hydroxyl radicals rather than than being quenched back to O. Calculate this at the ground with a temperature of 300 K and 100 percent humidity (water vapor pressure equals 35 hPa), and at 30 km with a temperature consistent with the JPL profile and 5 ppmv (parts per million) of water vapor.
(ii) What is the O_x lifetime associated with $\text{O}^1\text{D} + \text{H}_2\text{O}$ at the two heights? For 30 km, assume the $J_{\text{O}_3 \rightarrow \text{O}^1\text{D}}$ value in JPL, and for the ground, extrapolate from 10 km.
12. A much higher percentage of the O^1D that is produced from O_3 photolysis is used to help produce OH near the surface than in the stratosphere. What is the main reason for this?

Oxidizing Power of the Troposphere: HO_x Partitioning (T2)

1. Shown below is a plot of model calculated HO_2 and OH concentrations at two latitudes versus the NO mixing ratio. Assume that CO and O_3 are kept constant while NO is varied. Assume that the reactions that determine the HO_x partitioning in the model are



$$[\text{M}] = 2.1 \times 10^{19} \frac{\text{molec}}{\text{cm}^3}$$

ozone mixing ratio = 60 ppb.

The pressure dependence of the second reaction has already been included in the rate constant.

(i) Calculate the lifetime of HO₂ with respect to NO and O₃ at 15 °N when the NO mixing ratio is 1 pptv.

(ii) Estimate the CO mixing ratio using the $\frac{HO_2}{OH}$ ratio at NO = 1 pptv and 15 °N.

2. (i) In the troposphere, OH concentrations typically increases with NO when the NO concentration is very low. What is the main reason for this?

(ii) How does this increase help explain the hemispheric asymmetry in OH concentrations?

(iii) What is the main reason HO_x concentrations decrease at large NO?

4. (i) What is the dominant sink of HO_x in the troposphere at low NO_x?

(ii) What is the dominant sink of HO_x in the troposphere at high NO_x?

5. What are the four main reactions which interconvert OH and HO₂ in the troposphere. (Two from OH to HO₂, and two from HO₂ to OH).

(ii) There are four different pathways using the above four reactions to go from OH to HO₂, then back to OH. Indicate these four cycles, and indicate which of them produces O₃, which destroys O₃, and which is neutral to O₃.

(iii) Which cycle would you expect to be dominate in a polluted area (i.e. near fossil fuel emissions).

(iv) Which cycle would you expect to be dominate in a pristine area (i.e. far from fossil fuel emissions).

7. (i) At low NO_x, emissions of NO into the atmosphere from pollution tends to increase OH. Explain using the relevant reactions.

(ii) At high NO_x, emissions of NO into the atmosphere from pollution tends to decrease OH. Explain using the relevant reactions.

8. Assume the following conditions: (If giving this again use HO₂ + HO₂ reaction as the dominant HO_x sink. Give formula for dependence of PSat on temp. Clarify M in OH + NO₂.)

Pressure = 1000 hPa

Temperature = 298 K

O₃ = 50 ppbv

CO = 80 ppbv

Relative humidity = 80 %.

$J_{O_3 \rightarrow O^1D+O_2} = 1 \times 10^{-5} \text{ sec}^{-1}$

$J_{NO_2} = 0.01 \text{ sec}^{-1}$

Assume the O¹D concentration can be calculated by assuming steady state between production from ozone photolysis, quenching by O₂ and N₂, and reaction with water vapor.

Assume the HO₂/OH ratio can be calculated according to steady state with HO₂ reacting with O₃ and NO, and OH reacting with O₃ and CO only.

Assume HO_x can be considered a family with O¹D + H₂O → the only HO_x source and OH + HO₂ → H₂O + O₂ and OH + NO₂ → HNO₃ the only HO_x sinks.

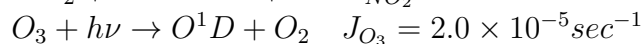
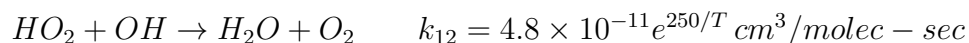
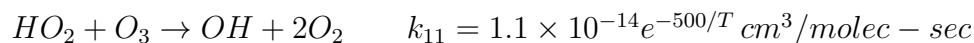
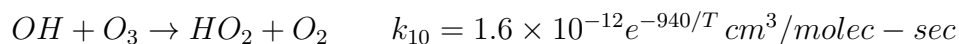
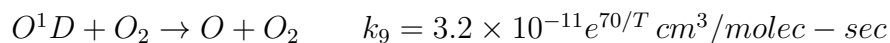
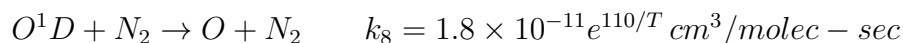
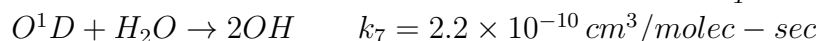
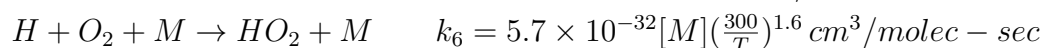
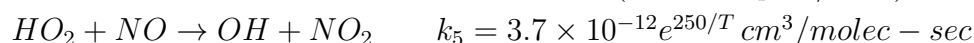
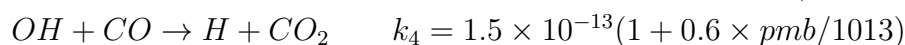
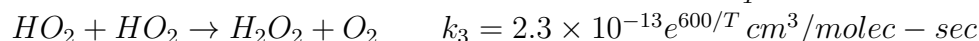
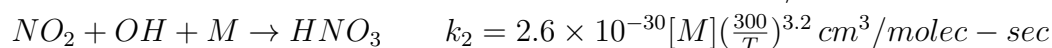
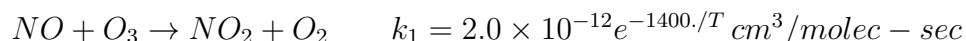
Assume that there is steady state relationship between NO and NO₂ formed by NO₂ photolysis and the reaction of NO with O₃.

In your plots assume a range of NO concentrations from 1 pptv to 10 ppbv. Use a logarithmic scale for NO.

- (i) What is the water vapor concentration?
- (ii) What is the concentration of O¹D?
- (iii) Derive an analytical expression for the dependence of HO₂/OH on NO.
- (iv) Plot the HO₂/OH ratio versus NO.
- (v) Derive an expression for NO₂ in terms of O₃, and J_{NO₂} and NO.
- (vi) Using steady state for HO_x, and HO_x family style approximations, solve for the concentration of OH and HO₂ versus NO.
- (vii) Plot the concentrations of OH and HO₂ versus NO. Use pptv for your units of OH and HO₂.
- (viii) It is really only valid to consider HO_x a family when the dominant sink of OH is conversion to HO₂. For what range of NO concentrations is this valid?

Oxidizing Power of the Troposphere: Ox Production (T3)

1. Why are ozone concentrations lower in the troposphere than the stratosphere? Give at least two reasons.
2. The reaction CH₃O₂ + NO is considered an ozone production reaction. Explain.
3. What are two reactions which are considered to destroy ozone in the troposphere?
4. O₃ concentrations tend to be low in the remote marine boundary layer. Give three reasons.
5. Consider the following reactions involving OH, HO₂, H₂O₂, O₃, NO, NO₂, H₂O, CO, H, O₂, O¹D, N₂, and O₂. (*Excessively complicated question that would not be directly asked on a quiz.*)



Also assume:

Temperature = 300 K

Pressure = 1013 hPa

O₃ = 50 ppbv

CO = 80 ppbv

[H₂O] = 0.01 [M] (ie. one part per hundred water vapor)

NO = 100 pptv

(i) Derive an expression for the HO₂/OH ratio from the above reactions, and evaluate it for the conditions listed. You can use family style approximations to partition HO_x (= H + OH + HO₂).

(ii) Calculate the OH and HO₂ mixing ratios (in pptv). You can assume the formation of HNO₃ and H₂O₂ are pure HO_x sinks (eg. are removed by rainout or surface deposition so don't photolyze to regenerate HO_x). You can also use family style approximations to partition NO_x (= NO + NO₂).

(iii) What are the four main terms in dO_3/dt in the above system of reactions.

(iv) Evaluate each of these four terms.

(v) What is the net rate of ozone production in ppbv/day?

6. At what time of year do Northern Hemisphere ozone concentrations at the surface typically peak. Give two reasons.

7. In the troposphere, net ozone production rates tend to be more positive in the upper troposphere than near the surface. Give a reason for this.

8. NO_x concentrations in remote regions of the equatorial Pacific are usually very small. In this problem, we assume that all NO_y species concentrations are zero. The concentrations of O₃, O, O¹D, H₂O, OH, HO₂, H, O₂, N₂, CO, and CO₂ are nonzero. Do not consider reaction rates or photolysis rates other than those listed below.

Pressure = 950 hPa

Temperature = 295 K

H₂O = 10000 ppmv

O₃ = 20 ppbv

CO = 70 ppbv

[N₂] = 0.79 [M]

[O₂] = 0.20 [M]

Photolysis Rates

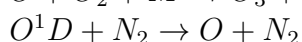
$$J_{O_3} = 6.0 \times 10^{-4} \text{sec}^{-1}$$

$$J_{O_3} = 2.0 \times 10^{-5} \text{sec}^{-1}$$

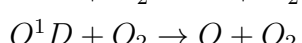
Reaction Rates



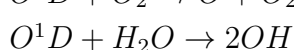
$$k_1 = 2.9 \times 10^{-15}$$



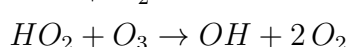
$$k_8 = 1.8 \times 10^{-11} e^{110/T} \text{ cm}^3/\text{molec} - \text{sec}$$



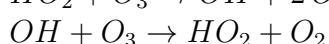
$$k_9 = 3.2 \times 10^{-11} e^{70/T} \text{ cm}^3/\text{molec} - \text{sec}$$



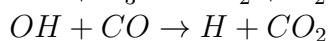
$$k_7 = 2.2 \times 10^{-10} \text{ cm}^3/\text{molec} - \text{sec}$$



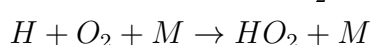
$$k_2 = 1.07 \times 10^{-15}$$



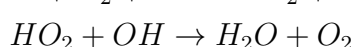
$$k_4 = 2.0 \times 10^{-14}$$



$$k_4 = 1.5 \times 10^{-13} (1 + 0.6 \times \text{pmb}/1013)$$



$$k_6 = 5.7 \times 10^{-32} [M] \left(\frac{300}{T}\right)^{1.6} \text{ cm}^3/\text{molec} - \text{sec}$$



$$k_{12} = 4.8 \times 10^{-11} e^{250/T} \text{ cm}^3/\text{molec} - \text{sec}$$

(i) What fraction of O¹D atoms react with H₂O?

(ii) What is the concentration of O¹D? Assume that the sources and sinks of O¹D are in steady state.

(iii) Use family style approximations to calculate the HO₂/OH ratio.

(iv) Use family style approximations to calculate the concentrations of OH and HO₂.

(v) Calculate the net rate of change of the ozone mixing ratio, in ppbv/day.

(vi) What is the lifetime of ozone?

9. This question is designed to show that net ozone production in the upper troposphere is generally positive, but that it is usually negative near the surface in the absence of elevated NO_x .

Surface case: $T = 300 \text{ K}$, pressure = 1000 hPa, $P_{\text{H}_2\text{O}} = 20 \text{ hPa}$, $[\text{M}] = 2.4 \times 10^{19} \text{ molec/cm}^3$.

Upper tropospheric case: $T = 220 \text{ K}$, pressure = 200 hPa, $P_{\text{H}_2\text{O}} = 0.05 \text{ hPa}$, $[\text{M}] = 6.6 \times 10^{18} \text{ molec/cm}^3$.

$[\text{NO}] = 50 \text{ pptv}$ in both cases.

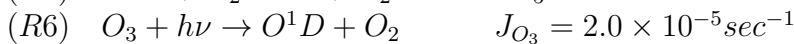
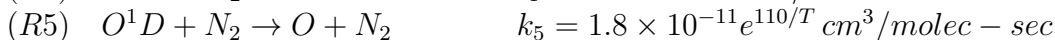
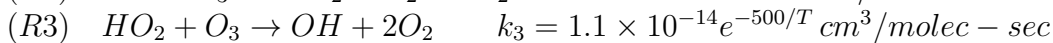
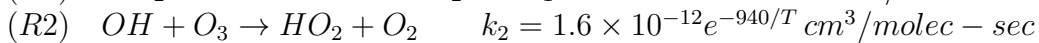
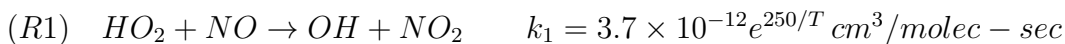
$[\text{CO}] = 80 \text{ ppbv}$ in both cases.

$[\text{O}_3] = 40 \text{ ppbv}$ in both cases.

It can be assumed that HO_x is in steady state with its sources and sinks, and can be partitioned using family style approximations.

It can be assumed that $[\text{O}^1\text{D}]$ is in steady state.

Assume the following reaction set:



(i) Solve for the $[\text{OH}]/[\text{HO}_2]$ ratio at the surface.

(ii) Solve for the $[\text{OH}]/[\text{HO}_2]$ ratio in the upper troposphere.

(iii) Solve for $[\text{O}^1\text{D}]$ at the surface.

(iv) Solve for $[\text{O}^1\text{D}]$ in the upper troposphere.

(v) In this reaction scheme, what reaction is the source of HO_x ?

(vi) In this reaction scheme, what reaction is the sink of HO_x ?

(vii) Solve for $[\text{HO}_2]$ at the surface.

(viii) Solve for $[\text{HO}_2]$ in the upper troposphere.

(ix) In this reaction scheme, what are the three reactions which are considered to destroy ozone.

(x) In this reaction scheme, what is the reaction which is considered to produce ozone?

(xi) Calculate the net ozone production rate (prod - loss) (ppbv/day) at the surface.

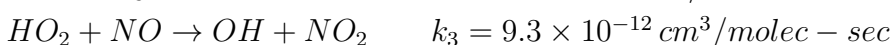
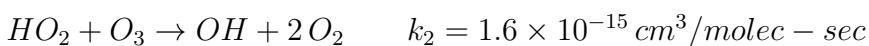
(xii) Calculate the net ozone production rate (ppbv/day) in the upper troposphere.

10. How might global warming affect the oxidizing capacity of the atmosphere (ie. levels of ozone or OH)? Again specify a reaction if possible.

13. This question involves estimating the number of molecules of ozone produced per CO oxidation. Assume every CO reacts with OH to produce HO_2 .



The HO_2 that is produced can react then with either NO or O_3 :



$[\text{M}] = 2 \times 10^{19} \text{ molec/cm}^3$

$\text{O}_3 : 50 \text{ ppbv}$

Assume that every NO_2 produced in the second reaction subsequently photolyzes to produce O , which then reacts with O_2 to produce O_3 .

(i) Write down the net rate of ozone production (i.e. production and destruction) associated with these reactions.

(i) Assume the O_3 mixing ratio is 50 ppbv. What is the mixing ratio of NO (in pptv) at which the net number of ozone molecules produced per CO oxidized is zero?

(ii) Assume an average NO mixing ratio in the troposphere of 100 pptv. How many molecules of ozone are produced per each CO oxidized?

(iii) Assume the mixing ratio of CO in the atmosphere is 80 ppbv, the NO mixing ratio is 10 pptv, and the OH mixing ratio is 1 pptv. what is the net impact in ppbv/day of CO oxidation on the rate of change of ozone?

(iv) The current direct emission of CO into the atmosphere is 4×10^{13} moles/year. Assuming an average NO mixing ratio in the troposphere of 100 pptv, how many moles of ozone are produced each year by CO oxidation?

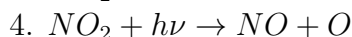
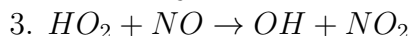
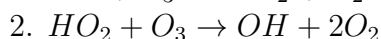
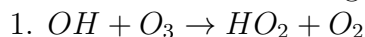
14. Suppose that there was no NO_x in the troposphere so that there was no way to produce ozone.

(i) What would then be the only source of ozone to the troposphere?

(ii) How would this impact the production of HO_x in the troposphere?

(iii) How would this impact the chemical composition of the troposphere? Give two examples.

15. Assume the following reactions:



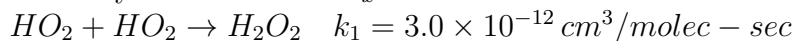
By imposing steady state conditions on various species, show that the net rate of O_x production by HO_x can be written,

$$d[\text{O}_x]/dt = - 2 k_2 [\text{HO}_2] [\text{O}_3]$$

Oxidizing Power of the Troposphere: Is O_x production Hydrocarbon or NO_x limited? (T4)

18. The average emission of NO_x over the continental United States is 2×10^{11} molecules $\text{cm}^{-2} \text{s}^{-1}$. Assume that all of this NO_x is oxidized and rains out over the United States. The rate of HO_x production P_{HO_x} is 4×10^6 molecules $\text{cm}^{-3} \text{s}^{-1}$.

The only two sinks of HO_x are:



The $[\text{M}]$ dependence has already been included in k_2 (i.e. do not need $[\text{M}]$.)

Model the United States as a well mixed box with a depth of 10 km. i.e. treat all quantities as independent of height.

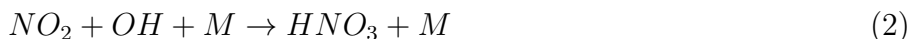
(i) What is the rate of HO_x destruction via reaction (2)?

(ii) What is the rate of HO_x destruction via reaction (1)?

(iii) Would you expect ozone production over the United States to be limited by the availability of NO_x or hydrocarbons? Explain.

(iv) Would you expect the mean OH concentration to increase or decrease in response to increased emissions of NO_x ? Explain.

19. (From Chapter 12 Introduction to Atmospheric Chemistry, by Daniel Jacob.) Model the lower troposphere over the eastern United States as a well-mixed box of height 2 km extending 1000 km in the east-west direction. The box is ventilated by a constant wind from the west with a speed of 2 m s⁻¹. The mean NO_x emission flux in the eastern United States is 2 × 10¹¹ molecules cm⁻² s⁻¹, constant throughout the year. Let P(HO_x) represent the production rate of HO_x in the region. As seen in this chapter, we can diagnose whether O₃ production in the region is NO_x - or hydrocarbon-limited by determining which one of the two sinks for HO_x, (1) or (2), is dominant:



We present here a simple approach for making this diagnosis. It is convenient to assume that the box has some width *w*. Refer to the height of the box (2 km) as *H*, and the length (1000 km) as *L*. Your answers should be independent of *w*.

The total volume is then $V = w \times H \times L$.

Define $F(NO_x)$ as the flux of NO_x at the bottom of the box (molec/cm²).

Define $L(NO_x)$ as the loss rate of NO_x (in molec/sec · cm²) in the box due to the formation of nitric acid.

Define $LT(NO_x)$ as the total number of NO_x molecules leaving the box by transport per second. Note that it has units of molec/sec, different from $L(NO_x)$.

(i) Express $LT(NO_x)$ in terms of the dimensions of the box, the horizontal wind speed *w*, and the NO_x concentration.

(ii) Assuming that the NO_x in the box is in steady state (ie. total flux of NO_x into the box per second = number of NO_x molecules chemically destroyed in the box per second + number NO_x transported out of the box per second), find the concentration of NO_x in the box. Assume that the NO_x emitted into the eastern United States has a lifetime of 12 hours against oxidation to HNO₃ by reaction (2). Assume reaction (2) to be the only sink for NO_x (a fair approximation during summer). Also assume that the NO_x concentration of the air entering the box is zero. When you write down the conservation equation, make sure that all the terms are dimensionally consistent.

(iii) Calculate the fraction of emitted NO_x that is oxidized within the region (vs. ventilated out of the region). You should find that most of the NO_x emitted in the eastern United States is oxidized within the region.

20. A photochemical model calculation indicates a 24-hour average HO_x production rate $P(HO_x) = 4 \times 10^6$ molecules cm⁻³ s⁻¹ over the eastern United States in July.

(i) Compare this source of HO_x to the source of NO_x.

(ii) Use the criteria given above to conclude as to whether O₃ production over the eastern United States in July is NO_x - or hydrocarbon-limited. You may assume that the only two sinks of HO_x are reactions (1) and (2) given above.

Oxidizing Power of the Troposphere: CO (T5)

1. (i) CO oxidation can produce O₃ in the troposphere. Write down the sequence of reactions by which this occurs.

(ii) Give a reason as to why this mechanism for O₃ production is not very important in the stratosphere.

2. The two principal sources of CO to the atmosphere are oxidation of CH₄ and combustion. Mean rate constants for oxidation of CH₄ and CO by OH in the troposphere are $k_1 = 2.5 \times 10^{-15} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ and $k_2 = 1.5 \times 10^{-13} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$. Observations indicate mean CO concentrations of 80 ppbv in the northern hemisphere and 50 ppbv in the southern hemisphere, and a globally uniform CH₄ mixing ratio of 1700 ppbv. Calculate the fraction of the CO source in each hemisphere contributed by the oxidation of CH₄. You can assume that CO is in steady state within each hemisphere, and that transport of CO between hemispheres is not important.

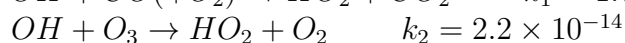
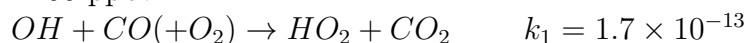
3. (i) One of the defining characteristics of the troposphere, as opposed to the stratosphere, is that OH is more likely to react with CO than O₃. Suppose that the O₃ mixing ratio was 50 ppbv (a typical tropospheric value). What is the CO mixing ratio at which OH will react with CO and O₃ with equal probability?

T = 220 K

Pressure = 220 hPa

[M] = $6.6 \times 10^{18} \text{molec/cm}^3$

O₃ = 50 ppbv



(ii) Given the usual range of tropospheric CO mixing ratios, would you expect OH to react more frequently with CO or O₃?

4. (i) What are two sources of methane to the troposphere?

(ii) CO concentrations tend to be higher in the Northern Hemisphere than the southern Hemisphere. Give a reason for this.

(iii) CO has a seasonal cycle in the Arctic in which it peaks around March and has a minimum around September. Give an explanation for this cycle in terms of the sources and sinks of CO.

5. (i) Show how the mixing ratios of O₃ (ozone) and CO (carbon monoxide) might typically vary with height between 0 and 20 km. Note the tropopause in both plots.

(ii) Changes in the O₃/CO ratio in going from the troposphere to the stratosphere have a big impact on how HO_x affects the ozone budget. Discuss briefly.

6. What are two source of carbon monoxide (CO)?

7. (i) Show how the mixing ratios of O₃ (ozone) and CO (carbon monoxide) might typically vary with height between 0 and 20 km. Note the tropopause in both plots.

(ii) Changes in the O₃/CO ratio in going from the troposphere to the stratosphere have a big impact on how HO_x affects the ozone budget. Discuss briefly.

8. In the troposphere CO and O₃ tend to be positively correlated in the summer, negatively correlated in the winter. Explain.

9. (i) In the troposphere, CO concentrations typically build up over the winter, peak in spring and decrease over the summer. With respect to the sources and sinks of CO, how would you explain this seasonal cycle?

(ii) How does the concentration of CO typically depend on latitude. Explain.

10. Plot how you would expect CO to vary over the course of a year at a mid-latitude location. Explain the increases and decreases.

11. Write down the sequence of reactions involved in the production of O₃ by CO oxidation in the troposphere.

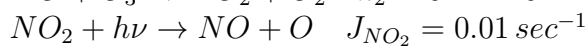
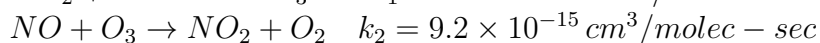
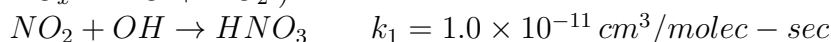
12. Simultaneous surface based measurements of CO and O₃ from Sable island show that CO and O₃ are positively correlated in the summer but negatively correlated in the winter. Explain.

Oxidizing Power of the Troposphere: NO_x Budget (T6)

13. What is an important natural source of NO_x to the troposphere?

14. (i) Model the lower atmosphere over the United States as a well-mixed box extending horizontally 5000 km in the west-east direction. There is a constant westerly wind blowing air through the box at U = 10 m/sec. What is the residence time of an air parcel in the box against removal by transport (in days)?

Assume the mean concentration of OH in the box is [OH] = 1.2 × 10⁶ molecules/cm³. Assume the following reactions, and that NO_x can be partitioned using family style approximations. (Remember NO_x = NO + NO₂.)



O₃ : 50ppbv

[M] = 2 × 10¹⁹ molec/cm³

(ii) Solve for the NO/NO₂ ratio.

(iii) What is the lifetime of an NO_x (= NO + NO₂) molecule in the box against conversion to HNO₃ (in days)?

(iv) What fraction of the NO_x emitted into the box from the surface will be removed by transport?

Chapter 12: Ozone Air Pollution (X12)

2. (i) Define ozone production efficiency ε (in both words and the chemical definition).

(ii) Plot how it depends on the NO_x concentration.

(iii) Suppose the NO_x emissions from a city were to double. Is this likely to double the production of ozone in that city? Explain.

3. (i) Show a contour plot of how ozone concentrations typically depend on emissions of NO_x (the x axis) and emissions of hydrocarbons (the y axis).

(ii) In the diagram, show the boundary between the NO_x limited and hydrocarbon-limited regimes, and label the two regimes.

(iii) In recent years, there has been an increased appreciation of the role of isoprene (a naturally emitted hydrocarbon) on ozone production in rural areas. How would the presence of isoprene change the sensitivity of ozone production to NO_x emissions. Would it tend to push ozone production into the NO_x or hydrocarbon limited regime? Explain.

5. High ozone episodes in cities tend to occur in summer. Why?

Chapter 13: Acid Rain (X13)

1. In general, would you expect an NO_x molecule to travel further before coming back to the surface as acid rain in the summer or winter? Explain.

2. The SO₂ and NO_x emissions of a power plant are making the rain in the area surrounding it more acidic. Will the affected region be larger in the summer than the winter, or vice versa?

3. (Problem 13.4 of Jacob) The southern San Joaquin Valley of California experiences extended stagnation episodes in winter due to strong and persistent subsidence inversions. These stagnation episodes are often accompanied by thick valley fogs. We use here a box model to describe the valley air during such a foggy stagnation episode. The top of the box is defined as the base of the inversion, 400 m above the valley floor. We assume no ventilation out of the box. The temperature of the box is 273 K.

(i) The major sources of pollution in the valley are steam generators for oil recovery, emitting SO_2 with a mean flux $E = 4 \times 10^2$ moles/ km^2 day $^{-1}$. This SO_2 is removed from the valley air by deposition to the surface (first order rate constant $k_d = 0.5$ day $^{-1}$) and by oxidation to H_2SO_4 (first order rate constant $k_0 = 1$ day $^{-1}$). Calculate the steady state SO_2 mixing ratio in the valley in units of ppbv. You can assume the SO_2 emission is everywhere instantly well mixed up to the base of the inversion layer (400 m). Compare to the U.S. air quality standards of 140 ppbv for 1-day exposure and 30 ppbv for 1-year exposure. Remember that at STP conditions, which you can assume here, 1 mole of air will occupy 22.4 litres, and 1 liter is 1000 cm^3 .

(i) Answer

There are lots of different ways to do the question. Here is one:

First convert the emission to an effective production equally spread from the ground to H (= 0.4 km)

$$P = E/H = 1000 \text{ moles SO}_2/\text{km}^3/\text{day}$$

At this point, the best thing to do is probably convert this P to moles SO_2 /moles air/day.

The number of moles of air in 1 km^3 can be obtained by

$$1 \text{ km}^3 = 1.0\text{E}+15 \text{ cm}^3 = 1.0\text{E}+12 \text{ liters}$$

1.0E+12 liters of air contains 4.46E+10 moles of air (dividing by 22.4).

$$\text{So } P = 2.2\text{E}-08 \text{ moles SO}_2/\text{moles air}/\text{day} = 22 \text{ ppbv SO}_2/\text{day}$$

Define C_{SO_2} as the SO_2 mixing ratio

At steady state,

$$dC_{\text{SO}_2}/dt = P - k_d C_{\text{SO}_2} - k_0 C_{\text{SO}_2} = 0$$

Solving for C_{SO_2} :

$$C_{\text{SO}_2} = P/(k_d + k_0) = (22 \text{ ppbv SO}_2/\text{day})/(1.5 \text{ 1}/\text{day}) = 14.7 \text{ ppbv SO}_2$$

This is lower than the U.S. air quality standard.

(ii) Sulfuric acid produced from SO_2 oxidation in the valley air is incorporated immediately into the fog droplets. These fog droplets are then removed from the valley air by deposition with a first-order rate constant $k'_d = 2$ day $^{-1}$. The liquid water content of the fog is 1×10^{-4} l water per m^3 of air. Calculate the steady-state fog water pH if H_2SO_4 is the only substance dissolved in the fog droplets. (Hint $\text{pH} = -\log [H^+]$, where $[H^+]$ is in moles per liter).

(ii) Answer

Let $C_{\text{H}_2\text{SO}_4}$ be the H_2SO_4 mixing ratio.

$$dC_{\text{H}_2\text{SO}_4}/dt = k_0 C_{\text{SO}_2} - k'_d C_{\text{H}_2\text{SO}_4} = 0$$

$$C_{\text{H}_2\text{SO}_4} = (k_0/k'_d) C_{\text{SO}_2} = (1/2) * 14.7 \text{ ppbv} = 7.4 \text{ ppbv}$$

Suppose you have 1 mole of air, or 22.4 litres.

In 1 m^3 of air, there is $1\text{E}-04$ liters of water.

$$1 \text{ m}^3 = 1\text{E}+06 \text{ cm}^3 = 1000 \text{ liters} = 44.6 \text{ moles}$$

So 1 mole of air will have $1\text{E}-04/(44.6) = 2.2\text{E}-06$ liters of water

So we have $7.4\text{E}-09$ moles of H_2SO_4 in $2.2\text{E}-06$ liters of water.

Each H_2SO_4 releases 2 H^+ (strong acid).

$$\text{Therefore } [H^+] = 2 * 7.4\text{E}-09 \text{ moles}/2.2\text{E}-06 \text{ liter} = 0.0067 \text{ moles/l}$$

This gives $\text{pH} = 2.2$

(iii) In fact the valley also contains large sources of ammonia from livestock and fertilized agriculture. The NH_3 emission flux is estimated to be $5.6 \times 10^2 \text{ moles/km}^2 \text{ day}^{-1}$. Is it enough to totally neutralize the H_2SO_4 produced from SO_2 emissions?

(iii) Answer

This does not involve a complex calculation.

Note that 2/3 of the emitted SO_2 is oxidized to H_2SO_4 .

But each H_2SO_4 produces 2 H^+ .

So the effective production of H^+ is $2 \cdot (2/3) \cdot 400 \text{ moles/km}^2/\text{day} = 533 \text{ moles/km}^2/\text{day}$

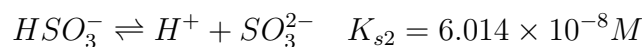
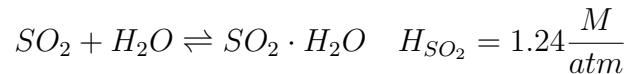
Each emitted NH_3 can neutralize one H^+ .

Since 560 is larger than 533, the emitted NH_3 can neutralize the H_2SO_4 .

4. Calculate the fraction of aqueous phase ammonia (ie. $\text{NH}_3 \cdot \text{H}_2\text{O} + \text{NH}_4^+$) to gaseous ammonia (NH_3) at a pH of 5.6 at a temperature of 273 K in a cloud of liquid water content $4 \times 10^{-6} \text{ cm}^3$ water per cm^3 air. Do the same for the cloud droplets with a pH of 3. You will first have to derive an expression for the pH dependent effective Henry's Law constant H^* for total dissolved ammonia.

5. What are two chemical species whose presence can help offset increased acidity in rainwater associated with enhanced atmospheric concentrations of NO_x and SO_2 . In each case, show the relevant reactions by which the concentration of $[\text{H}^+]$ in cloud or rainwater is reduced.

6. The gas phase mixing ratio of SO_2 in an air parcel is 2 ppbv. After a cloud forms, the mixing ratio of SO_2 decreases as some of the SO_2 enters the cloud droplets. Inside the cloud droplet, and equilibrium between $\text{SO}_2 \cdot \text{H}_2\text{O}$, HSO_3^- , and SO_3^{2-} , is quickly established. The solubility of SO_2 in water is determined by the following:



Define:

$$[\text{S(IV)}] = [\text{SO}_2 \cdot \text{H}_2\text{O}] + [\text{HSO}_3^-] + [\text{SO}_3^{2-}]$$

Then Henry's Law can be expressed:

$$[\text{S(IV)}] = H^* P_{\text{SO}_2},$$

where,

$$H^* = H \left[1 + \frac{K_{s1}}{[\text{H}^+]} + \frac{K_{s1}K_{s2}}{[\text{H}^+]^2} \right]$$

and

$$\text{pH} = -\log[\text{H}^+].$$

Also note that the ideal gas law can be expressed

$$PV = nRT,$$

where P is the pressure in atm, V is the volume in liters, n is the number of moles, the ideal gas constant $R = 0.082 \frac{\text{atm}}{\text{M}\cdot\text{K}}$.

(i) Find the gas phase mixing ratio of SO_2 in the cloud. Assume the pressure is 500 hPa, or 0.5 atm, that the temperature is 250 K, the cloud liquid water fraction = 1×10^{-7} , and the pH of the cloud droplets is 2.

(ii) Assume instead that the pH of the cloud droplets is 5. What is the gas phase mixing ratio of SO_2 ?

7. The rate of aqueous phase S(IV) oxidation by hydrogen peroxide is given by

$$-\frac{d[S(\text{IV})]}{dt} = \frac{k[H^+][\text{H}_2\text{O}_2][S(\text{IV})]\alpha_1}{1 + K[H^+]},$$

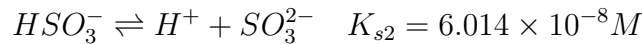
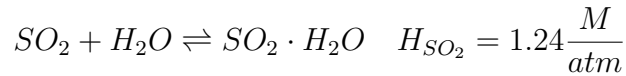
where,

$$k = 7.45 \times 10^7 \text{ M sec}^{-1}$$

$$K = 13 \text{ M}^{-1}$$

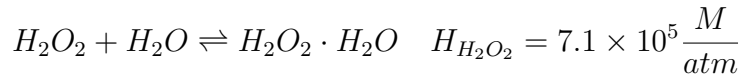
$$\alpha_1 = \frac{[\text{HSO}_3^-]}{[S(\text{IV})]}.$$

The solubility of S(IV) in water is determined in part by the following reactions.



Also,

$$\text{pH} = -\log[H^+]$$



Assume that a cloud of liquid water content $L = 10^{-7}$, contains 20 ppbv of gas phase SO_2 , and 6 ppbv of total H_2O_2 . The cloud has a pH of 5. By total is meant the sum of the actual gas phase mixing ratio of H_2O_2 plus what the contribution of aqueous phase H_2O_2 to the gas phase would be after conversion from molarity to mixing ratio. The ideal gas constant is $R = 0.082 \frac{\text{atm}}{\text{M}\cdot\text{K}}$. The pressure is 1 atm and the temperature 298 K.

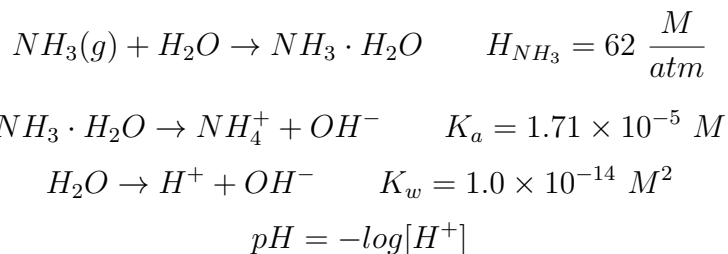
(a) Calculate $[\text{H}_2\text{O}_2]$, the molarity of hydrogen peroxide in the liquid phase.

(b) Calculate $[S(\text{IV})]$ and α_1 .

(c) Calculate the lifetime of an aqueous phase hydrogen peroxide molecule with respect to the loss by oxidation of S(IV). Convert this to a lifetime for total H_2O_2 . Are the losses of H_2O_2 via gas phase photolysis and attack by OH likely to be important processes within the cloud?

8. Give one of the chemical reaction(s), or series of chemical reactions, by which dust, or an "agricultural emission", increases the pH of rain.

9. The gas phase concentration of ammonia (NH_3) at the ground is 5 ppbv. Calculate the pH of a water droplet near the ground if ammonia is the only soluble gas phase species present. The temperature is 298 K.



10. The presence of ammonia (NH_3) in a cloud can increase the rate of aqueous phase oxidation of S(IV) to S(VI). Explain.

Glossary for Atmospheric Chemistry

Nitrogen:

Nitrogen N_2
Nitric Oxide NO
Nitrogen Dioxide NO_2
Nitric Acid HNO_3
atomic Nitrogen N
Nitrous Oxide N_2O

Hydrogen:

atomic hydrogen H
water H_2O
Hydroxyl radical OH
Peroxy radical HO_2
Hydrogen Peroxide H_2O_2

Chlorine:

Chlorine Monoxide Cl
Chlorine Dimer Cl_2O_2
Chlorine Nitrate ClONO_2
Hydrochloric Acid HCl
CFC's eg CFCl_3 , etc.

Methane and its products:

Methane CH_4
Methyl CH_3
Methyl Peroxy CH_3O_2
Formaldehyde CH_2O
Carbon Monoxide CO
Carbon Dioxide CO_2
Ethane C_2H_6

Oxygen:

Oxygen O_2
Atomic Oxygen O
Excited Atomic Oxygen O^1D
Ozone O_3

Various:

Dimethyl Sulphide $(CH_3)_2S$
Sulphuric Acid H_2SO_4
Sulphur Dioxide SO_2
Hydrocarbon methane, ethane, etc.
PSC Polar Stratospheric Cloud