

SOLUTIONS TO PROBLEMS

**INTRODUCTION TO
ATMOSPHERIC CHEMISTRY**

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SOLUTIONS TO PROBLEMS, CHAPTER 1

1. 1 Fog formation

1. The saturation vapor pressure of water at 293 K is $P_{H_2O,SAT} = 23$ hPa. At sunset the air is at 50% relative humidity, therefore $P_{H_2O} = 11.5$ hPa. The dew point corresponding to this water vapor pressure is 282 K. The air must cool to 282 K in order for fog to form.

2. From the phase diagram we find that the stable phase of water is liquid. The fact that the atmosphere contains water vapor simply means that it is not in equilibrium. Under these conditions water will condense to produce a liquid phase, and P_{H_2O} will decrease until the gas-liquid equilibrium line is reached. Under isothermal conditions (20°C) equilibrium will be reached for $P_{H_2O, SAT} = 23$ hPa, so that 77% of the water vapor initially present will have condensed.

1. 2 Phase of water in a cloud

The saturation vapor pressure at 273 K is $P_{H_2O,SAT} = 6$ hPa. The corresponding mass concentration ρ_{H_2O} is

$$\rho_{H_2O} = \frac{M_{H_2O} P_{H_2O}}{RT} = \frac{18 \times 10^{-3} \cdot 6 \times 10^2}{8.31 \cdot 273} = 4.8 \times 10^{-3} \text{ kg m}^{-3} = 4.8 \text{ g m}^{-3}$$

Considering that cloud liquid water contents are in the range 0.1-1 g m⁻³, we conclude that most of the water in a cloud is present as vapor.

1. 3 The ozone column

1. At the peak of the ozone layer, $n_{O_3} = 5 \times 10^{12}$ molecules cm⁻³. The density of air at that altitude is

$$n_a = \frac{A_V P}{RT} = \frac{6.022 \times 10^{23} \cdot 35 \times 10^2}{8.31 \cdot 220} = 1.2 \times 10^{24} \text{ molecules m}^{-3} = 1.2 \times 10^{18} \text{ molecules cm}^{-3}$$

and the corresponding O₃ mixing ratio is $C_{O_3} = n_{O_3}/n_a = 4.2$ ppmv = 4200 ppbv. This is fifty times the O₃ air quality standard for surface air!

2. In surface air, $n_{O_3} = 1 \times 10^{12}$ molecules cm⁻³. The density of air at that altitude is

$$n_a = \frac{A_V P}{RT} = \frac{6.022 \times 10^{23} \cdot 1000 \times 10^2}{8.31 \cdot 300} = 2.4 \times 10^{25} \text{ molecules m}^{-3} = 2.4 \times 10^{19} \text{ molecules cm}^{-3}$$

and the corresponding O₃ mixing ratio is $C_{O_3} = n_{O_3}/n_a = 42$ ppbv, which is in compliance with the O₃ air quality standard. The relative decrease of C_{O_3} from 25 to 0 km is much larger than the relative decrease of n_{O_3} because of the change in atmospheric pressure:

$$\frac{C_{O_3}(z_2)}{C_{O_3}(z_1)} = \frac{n_{O_3}(z_2)}{n_{O_3}(z_1)} \cdot \frac{n_a(z_1)}{n_a(z_2)} = \frac{n_{O_3}(z_2)}{n_{O_3}(z_1)} \cdot \frac{P(z_1)T(z_2)}{P(z_2)T(z_1)} = 0.048 \frac{n_{O_3}(z_2)}{n_{O_3}(z_1)} \text{ between 0 and 25 km}$$

3. The O₃ column C is the total number of O₃ molecules per unit area of Earth's surface:

$$C = \int_0^{\infty} n_{O_3} dz$$

For the triangular function proposed here as an approximation to the O_3 profile, the integral is simply the area of the triangle ($1/2 \times \text{base} \times \text{height}$). We carry out the numerical calculation in SI units:

$$\frac{1}{2} \times (30 \text{ km}) \times (5 \times 10^{12} \text{ molecules cm}^{-3}) = 0.5 \cdot 30 \times 10^3 \cdot 5 \times 10^{18} = 7.5 \times 10^{22} \text{ molecules m}^{-2}$$

4. Consider the above O_3 column brought to sea level as a layer of unit horizontal area A and vertical thickness h (volume $V = Ah$) at $P = 1.013 \times 10^5 \text{ Pa}$, $T = 273 \text{ K}$. The column contains 7.5×10^{22} molecules, corresponding to $N = 7.5 \times 10^{22} / 6.022 \times 10^{23} = 0.125$ moles. Apply the ideal gas law to obtain h :

$$PV = NRT \Rightarrow h = \frac{NRT}{PA} = \frac{0.125 \cdot 8.31 \cdot 273}{1.013 \times 10^5 \cdot 1} = 2.8 \times 10^{-3} \text{ m} = 2.8 \text{ mm}$$

SOLUTIONS TO PROBLEMS, CHAPTER 2

2. 1 Scale height of the Martian atmosphere

$$H = \frac{RT}{M_a g} = \frac{8.31 \cdot 220}{44 \times 10^{-3} \cdot 3.7} = 11.2 \text{ km}$$

which is larger than the scale height of the Earth's atmosphere. The atmosphere of Mars extends deeper than that of the Earth because of the smaller size of Mars and hence its weaker gravitational pull on its atmosphere.

2. 2 Scale height and atmospheric mass

1. The mass dm of the species in an elementary slab of atmosphere of unit area and vertical thickness dz is $dm = \rho(z)dz$. We integrate over the depth of the atmosphere and over the area A of the Earth:

$$m = A \int_0^{\infty} \rho(z) dz = A \int_0^{\infty} \rho(0) e^{-\frac{z}{h}} dz = -A\rho(0)he^{-\frac{z}{h}} \Big|_0^{\infty} = A\rho(0)h \quad (1)$$

2.1 From the ideal gas law:

$$\rho_a = \frac{M_a P}{RT}$$

where $M_a = 0.029 \text{ kg/mol}$; $T = 288 \text{ K}$; and $P = 9.84 \times 10^4 \text{ Pa}$. We use SI units for all quantities to avoid unit conversion mistakes. In this manner we obtain

$$\rho_a = \rho(0) = \frac{\left(0.029 \frac{\text{kg}}{\text{mol}}\right)(9.84 \times 10^4 \text{ Pa})}{\left(8.31 \frac{\text{J}}{\text{mol} \cdot \text{K}}\right)(288 \text{ K})} = 1.19 \frac{\text{kg}}{\text{m}^3}$$

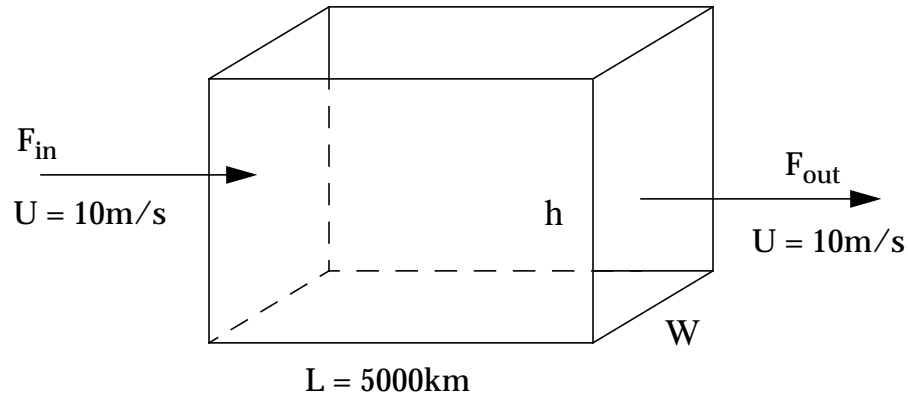
2.2 We substitute in equation (1) $A = 4\pi R^2 = 5.1 \times 10^{14} \text{ m}^2$, where $R = 6400 \text{ km}$ is the radius of the Earth; $\rho(0) = 1.19 \text{ kg m}^{-3}$; and the atmospheric scale height is $h = 7.4 \times 10^3 \text{ m}$. The resulting mass of the atmosphere is $m = 4.4 \times 10^{18} \text{ kg}$, somewhat lower than the value of $5.2 \times 10^{18} \text{ kg}$ derived in the text. The reason for the difference lies in the assumption $\rho \sim P$ made when applying the barometric law to air density. In fact $\rho \sim P/T$ (ideal gas law); as z increases and T decreases, $\rho(z)$ deviates upward from the value $\rho(0)\exp(-z/h)$ predicted from the barometric law and hence equation (1) underestimates m .

3.1 We apply equation (1) to sea salt, taking into consideration that sea salt is emitted over only 70% of the globe.

$$m_{ss} = 0.70 A \rho_{ss}(0) h_{ss} = (0.70)(5.1 \times 10^{14} \text{ m}^2) \left(10 \times 10^{-9} \frac{\text{kg}}{\text{m}^3}\right) (500 \text{ m}) = 1.8 \times 10^9 \text{ kg}$$

SOLUTIONS TO PROBLEMS, CHAPTER 3

3. 1 Ventilation of pollution from the United States

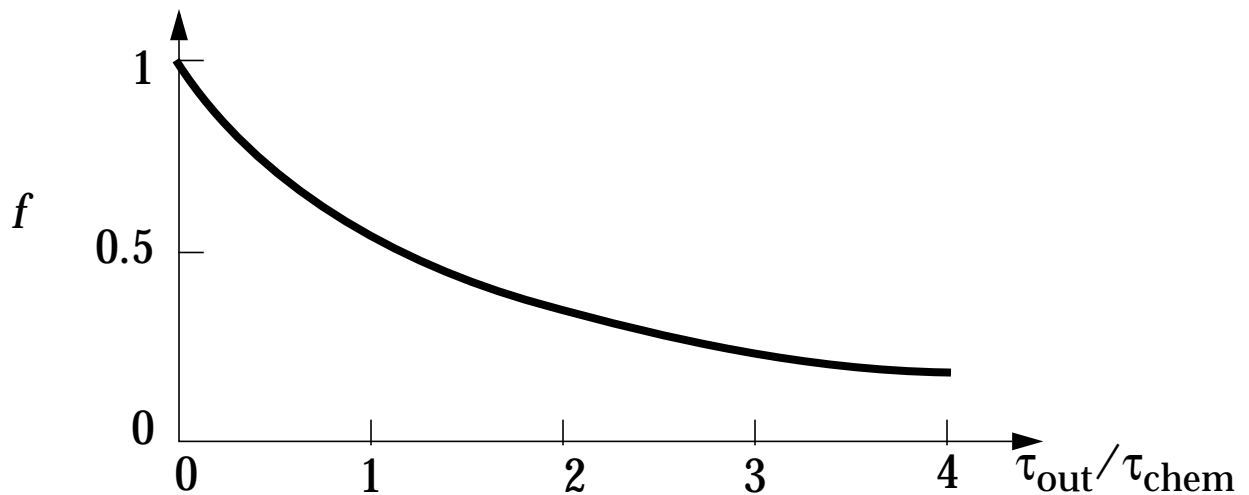


1. Let W and h represent the width and height of the box respectively. The volume of the box is LWh . In one unit time a volume UWh of air flows out of the box. The residence time of air in the box is therefore:

$$\tau_{out} = \frac{LWh}{UWh} = \frac{L}{U} = \frac{5 \times 10^6}{10} = 5 \times 10^5 \text{ s} = 5.8 \text{ days}$$

2. Let m represent the mass of the pollutant in the United States box. The pollutant is removed by chemical loss (time constant τ_{chem} , loss rate m/τ_{chem}) and export out of the box (time constant τ_{out} , loss rate m/τ_{out}). The fraction f of the pollutant removed by export is

$$f = \frac{\text{export loss rate}}{\text{total loss rate}} = \frac{\frac{m}{\tau_{out}}}{\frac{m}{\tau_{chem}} + \frac{m}{\tau_{out}}} = \frac{1}{1 + \frac{\tau_{out}}{\tau_{chem}}}$$



The efficiency with which a pollutant emitted from the United States is exported to the global atmosphere

depends on its rate of chemical loss relative to the rate of ventilation. For the typical wind speed considered here, pollutants with lifetimes longer than 6 days against chemical loss are efficiently exported out of the United States ($f > 0.5$) while pollutants with shorter lifetimes are mostly removed within the United States and have relatively little global impact.

3. 2 Stratosphere-troposphere exchange

1. The ^{90}Sr inventories in the stratosphere and troposphere are affected by loss from radioactive decay (L), transfer from the stratosphere to the troposphere (F_{ST}), reverse transfer from the troposphere to the stratosphere (F_{TS}), and deposition (D). Deposition applies only in the troposphere. There were no ^{90}Sr emissions during the post-1962 period. The mass balance equations are:

$$\frac{dm_S}{dt} = F_{TS} - F_{ST} - L_S$$

$$\frac{dm_T}{dt} = F_{ST} - F_{TS} - L_T - D$$

The transfer rates F_{ST} and F_{TS} are related to the transfer rate constants k_{ST} and k_{TS} :

$$F_{ST} = k_{ST}m_S$$

$$F_{TS} = k_{TS}m_T$$

The loss rates from radioactive decay are

$$L_S = k_d m_S$$

$$L_T = k_d m_T$$

Here k_d is the rate constant for radioactive decay; $k_d = \ln 2 / t_{1/2} = 0.025 \text{ yr}^{-1}$, where $t_{1/2} = 28 \text{ yr}$ is the half-life of ^{90}Sr .

The loss rate from deposition is

$$D = k_D m_T$$

Here k_D is the loss rate constant for deposition; $k_D = 1/\tau_D = 0.1 \text{ day}^{-1}$ where $\tau_D = 10 \text{ days}$ is the lifetime against deposition in the troposphere.

Replacing in the mass balance equations:

$$\frac{dm_S}{dt} = k_{TS}m_T - (k_{ST} + k_d)m_S$$

$$\frac{dm_T}{dt} = k_{ST}m_S - (k_{TS} + k_d + k_D)m_T$$

2. Assuming that transfer of ^{90}Sr from the troposphere to the stratosphere (F_{TS}) is negligible, the mass balance equation for m_S becomes

$$\frac{dm_S}{dt} = -(k_{ST} + k_d)m_S$$

Integrating this equation yields:

$$m_S(t) = m_S(0)e^{-(k_{ST} + k_d)t}$$

Comparing to the observed decrease

$$m_S(t) = m_S(0)e^{-kt}$$

with $k = 0.77 \text{ yr}^{-1}$, we obtain:

$$k_{ST} = k - k_d$$

so that $k_{ST} = 0.75 \text{ yr}^{-1}$ and hence $\tau_S = 1/k_{ST} = 1.3 \text{ yr}$. Note that radioactive decay has negligible effect on the calculation of τ_S because the lifetime of ^{90}Sr against radioactive decay is long compared to the residence time of air in the stratosphere.

3. Total air mass must be at steady state between the troposphere and the stratosphere,

$$m_S' k_{ST} = m_T' k_{TS}$$

and therefore

$$\tau_T = \tau_S \left(\frac{m_T'}{m_S'} \right)$$

Since the pressure at a given altitude is proportional to the mass of atmosphere overhead,

$$\frac{m_T'}{m_S'} = \frac{P_{\text{surface}} - P_{\text{tropopause}}}{P_{\text{tropopause}} - P_{\text{stratopause}}}$$

where $P_{\text{surface}} = 1000 \text{ hPa}$, $P_{\text{tropopause}} = 150 \text{ hPa}$, $P_{\text{stratopause}} = 1 \text{ hPa}$. We find $m_T'/m_S' = 5.7$ and hence $\tau_T = 7.4 \text{ years}$. Compare to the lifetime $\tau_D = 10 \text{ days}$ of ^{90}Sr against deposition in the troposphere; the fraction of ^{90}Sr in the troposphere that is transferred back to the stratosphere is negligible, justifying our assumption in question 2.

4. Let m represent the mass of HCFC in the troposphere. The HCFC loss rate by transfer to the stratosphere is $L_{TS} = m/\tau_T$, while the loss rate from oxidation is $L_{ox} = m/\tau_{ox}$ where τ_{ox} is the lifetime against oxidation. The fraction f of emitted HCFC that penetrates the stratosphere is

$$f = \frac{L_{TS}}{L_{TS} + L_{ox}} = \frac{\frac{1}{\tau_T}}{\frac{1}{\tau_T} + \frac{1}{\tau_{ox}}} = \frac{1}{1 + \frac{\tau_T}{\tau_{ox}}}$$

For HCFC-123, $\tau_{ox} = 1.4 \text{ years}$ and $f = 0.16$; for HCFC-124, $\tau_{ox} = 5.9 \text{ years}$ and $f = 0.44$.

3. 3 Interhemispheric exchange

1. We write mass balance equations for m_N and m_S , and take the difference:

$$\frac{dm_N}{dt} = E + km_S - km_N - k_c m_N$$

$$\frac{dm_S}{dt} = km_N - km_S - k_c m_S$$

$$\frac{d(m_N - m_S)}{dt} = E - (2k + k_c)(m_N - m_S)$$

In 1983, $m_N - m_S = 7\text{kg}$, $E=15\text{ kg}$; assuming steady state for $(m_N - m_S)$ we obtain

$$(2k + k_c) = \frac{E}{(m_N - m_S)}$$

$$k = \frac{1}{2} \left(\frac{E}{m_N - m_S} - k_c \right) = 1.04 \text{ yr}^{-1}$$

$$\tau = 1/k = .96 \text{ yr}$$

2. Based on the equation:

$$\frac{d(m_N - m_S)}{dt} = E - (2k + k_d)(m_N - m_S)$$

we see that the time scale for $(m_N - m_S)$ to relax to steady state is $1/(2k+k_d) = 0.5\text{ yr}$. The rise in E is slow relative to this time scale so that $(m_N - m_S)$ has the time to continually adjust to steady state as E increases.

3. 4 Long-range transport of acidity

We start from the puff model versions of the mass balance equations for SO_2 and H_2SO_4 :

$$\frac{d[\text{SO}_2]}{dt} = -k_1[\text{SO}_2]$$

$$\frac{d[\text{H}_2\text{SO}_4]}{dt} = k_1[\text{SO}_2] - k_2[\text{H}_2\text{SO}_4]$$

Integration of the mass balance equation for SO_2 yields as solution

$$[\text{SO}_2] = [\text{SO}_2]_o e^{-k_1 t}$$

Replacing into the mass balance equation for H_2SO_4 :

$$\frac{d[\text{H}_2\text{SO}_4]}{dt} + k_2[\text{H}_2\text{SO}_4] = k_1[\text{SO}_2]_o e^{-k_1 t} \quad (1)$$

We seek the general solution to (1) as the sum of the general solution to the homogeneous equation (right-hand-side equal zero) and a particular solution to the full equation (1). The general solution to the homogeneous equation is

$$[\text{H}_2\text{SO}_4] = A e^{-k_2 t}$$

where A is an integration constant. In addition, we can see from the form of (1) that it must admit a solution of the form $B\exp(-k_1t)$ where B is a constant to be determined by substitution in the mass balance equation: we find $B = [\text{SO}_2]_0 / (k_2 - k_1)$. The general solution to (1) is therefore:

$$[\text{H}_2\text{SO}_4] = Ae^{-k_2t} + \frac{k_1[\text{SO}_2]_0}{k_2 - k_1}e^{-k_1t}$$

We derive the value of the integration constant A from the initial condition $[\text{H}_2\text{SO}_4]_0 = 0$ at $t = 0$:

$$A = -\frac{k_1[\text{SO}_2]_0}{k_2 - k_1}$$

and thus obtain the final solution for $[\text{H}_2\text{SO}_4]$:

$$[\text{H}_2\text{SO}_4] = \frac{k_1[\text{SO}_2]_0}{k_2 - k_1}(e^{-k_1t} - e^{-k_2t})$$

To obtain the solutions as a function of distance downwind of the power plants we simply replace $t = x/U$ in the expressions for $[\text{SO}_2]$ and $[\text{H}_2\text{SO}_4]$.

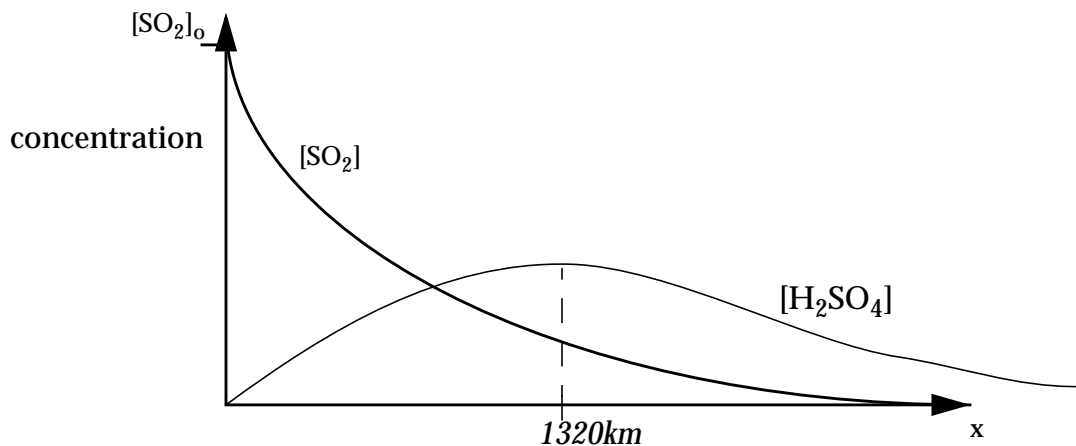
The rate of acid deposition is $k_2[\text{H}_2\text{SO}_4]$ where k_2 is taken to be constant; thus the maximum in acid deposition corresponds to the maximum in $[\text{H}_2\text{SO}_4]$. Solving for $d[\text{H}_2\text{SO}_4]/dt = 0$,

$$\frac{d}{dt}[\text{H}_2\text{SO}_4] = \frac{k_1[\text{SO}_2]_0}{k_2 - k_1}(-k_1e^{-k_1t} + k_2e^{-k_2t})$$

yields

$$t_{max} = \frac{\ln\left(\frac{k_1}{k_2}\right)}{k_1 - k_2}$$

so that $t_{max} = 3.1$ days and $x_{max} = ut_{max} = 1300$ km. Acid deposition is maximum 1300 km northeast of the power plants, i.e., somewhere over eastern Canada.



3.5 Box vs. column model for an urban airshed

a) Steady-state box model:

Source of X (emission) = E/h (molecules $\text{cm}^{-3} \text{s}^{-1}$)

Sink of X (transport out) = $U[X]/L$ (molecules $\text{cm}^{-3} \text{s}^{-1}$)

Source = Sink: $E/h = U[X]/L \Rightarrow [X] = EL/Uh$

b) Column model: consider an air column of height h traveling at a wind speed U through the urban area from $x = 0$ to $x = L$. Over the urban area the source of X in the column is E/h , and there is no sink:

$$\frac{d[X]}{dt} = \frac{E}{h}$$

Replacing $dt = dx/U$, and integrating:

$$U \frac{d[X]}{dx} = \frac{E}{h} \Rightarrow d[X] = \frac{E}{Uh} dx \Rightarrow [X] = \frac{Ex}{Uh}$$

Since this is a linear function the mean value of $[X]$ in the urban air is the value at $x = L/2$, i.e., $[X] = EL/2Uh$.

Thus the mean concentration in the column model is only half of that in the box model. The reason is that in the box model the residence time of X in the urban area is $\tau = L/U$ while in the column model it is $\tau = L/2U$ (representing the residence time of a molecule of X emitted as the column has already moved halfway across the urban area).

3.7 The Montreal protocol

1. The mass balance equation for CFC-12 is

$$\frac{dm}{dt} = E - km$$

where $k = 0.01 \text{ yr}^{-1}$ is the rate constant for photolysis. The time-dependent solution is:

$$m(t) = m(0)e^{-kt} + \frac{E}{k}(1 - e^{-kt})$$

and the steady-state solution is

$$m(\infty) = \frac{E}{k}$$

In the original Montreal protocol, emissions were to stabilize at 50% of 1989 values: $E = 0.5 \times 4 \times 10^8 = 2 \times 10^8 \text{ kg yr}^{-1}$. The resulting steady-state atmospheric mass of CFC-12 would be $m(\infty) = 2 \times 10^{10} \text{ kg}$, higher than the 1989 value. The 1989 value was far below the corresponding

steady state ($m(\infty) = 4 \times 10^{10}$ kg for $E = 4 \times 10^8$ kg yr⁻¹), because emissions were increasing rapidly.

2. Amended Montreal protocol. For the 1989-1996 period ($t = 7$ years), $m(0) = 1.0 \times 10^{10}$ kg and $E = 4 \times 10^8$ kg yr⁻¹. Substituting in the above time-dependent equation, we find the atmospheric mass of CFC-12 in 1996: $m = 1.2 \times 10^{10}$ kg.

For the 1996-2050 period ($t = 54$ years), $m(0) = 1.2 \times 10^{10}$ kg and $E = 0$. We find $m = 7.0 \times 10^9$ kg in 2050, or 70% of the 1989 value.

For the 2050-2100 period ($t = 50$ years), $m(0) = 7.0 \times 10^9$ kg and $E = 0$. We find $m = 4.2 \times 10^9$ kg in 2100, or 40% of the 1989 value.

3. Delayed-action scenario: for the 1989-2006 period ($t = 17$ years), $m(0) = 1.3 \times 10^{10}$ kg and $E = 4 \times 10^8$ kg yr⁻¹, we find $m = 1.5 \times 10^{10}$ kg.

For the 2006-2050 period (44 years), $m(0) = 1.5 \times 10^{10}$ kg and $E = 0$. We find $m = 1.0 \times 10^{10}$ kg in 2050.

For the 2050-2100 period (50 years), $m(0) = 1.0 \times 10^{10}$ kg and $E = 0$. We find $m = 0.61 \times 10^{10}$ kg in 2100.

The cost of a 10-year delay in regulation is almost 50 years in results!

SOLUTIONS TO PROBLEMS, CHAPTER 4

4. 1 Dilution of power plant plumes

1-C (unstable); 2-D (inversion); 3-A (unstable below stack, stable above); 4-B (stable below stack, unstable above)

4. 2 Short questions on atmospheric transport.

1. During summer, surface heating of the Earth's surface allows for deeper convection than in winter. Vertical ventilation of pollution is therefore faster than in winter. In winter, stronger thermal contrast (and hence stronger pressure gradient) between the tropics and the poles leads to stronger westerly winds at midlatitudes based on geostrophic balance. Horizontal ventilation of pollution is therefore faster than in summer.

2. Solar heating of the surface creates unstable conditions in the lower atmosphere. In an unstable atmosphere, both upward and downward motions are accelerated by buoyancy; both upward and downward transport of pollutants is therefore facilitated.

3. In the turbulent diffusion parameterization of turbulence, the flux $F = -KNdC/dz$ transports the pollutant always from regions of higher concentrations to regions of lower concentrations. For a pollutant emitted at the surface, the pollutant flux $F = -KNdC/dz$ must be upward and hence the mixing ratio must decrease with altitude (dC/dz must be negative). This result is consistent with the profile measured on day 1 but not with the profile measured on day 2. The profile on day 2 can be explained by rapid vertical pumping of pollutant to high altitudes by deep convection somewhere upwind of the measurement site.

4. At night, the stability of the atmosphere prevents pollution emitted at 200 m altitude from reaching the surface. In early morning, solar heating of the surface gradually erodes the nighttime stability; the unstable mixed layer eventually reaches 200 m altitude at which point pollution from the power plant is brought down to the surface. As daytime heating continues the mixed layer grows, diluting the pollution from the power plant. The maximum surface concentrations are therefore in early morning when the mixed layer first reaches 200 m altitude.

5. Adiabatic sinking of a cloudy air parcel causes it to heat. The resulting evaporation of cloudwater consumes part of that heat. This process is exactly the reverse of the condensation of water in a rising air parcel, and the lapse rate Γ_W is the same in both cases. Thus a sinking cloudy air parcel accelerates in a conditionally unstable atmosphere ($-dT/dz > \Gamma_W$). In a deep convective cloud system, such as a thunderstorm, this mechanism allows rapid transport of air from the upper to the lower troposphere.

6. The turbulent flux is proportional to the concentration gradient: $F = -KN\partial C/\partial z$. For a well-mixed gas $\partial C/\partial z = 0$ and hence the turbulent flux is zero.

4. 3 Seasonal motion of the ITCZ

We define a meteorological "northern hemisphere" as the world north of the ITCZ. Between January and July, air from the meteorological northern hemisphere is transferred to the meteorological southern hemisphere as the ITCZ moves north. From July to January the meteorological northern hemisphere expands, incorporating air from the meteorological southern hemisphere. The mass of air transferred from the meteorological northern to southern hemisphere between January and July is that contained in the band extending from latitude 5°S (λ_1) to 10°N (λ_2). We can assume that the mass of air in the band is

proportional to the surface area of the band since surface pressures are relatively uniform. The area of an elementary band $[\lambda, \lambda+d\lambda]$ is $2\pi R^2 \cos\lambda d\lambda$ (simple geometry). By integration, the area of a finite band $[\lambda_1, \lambda_2]$ is $2\pi R^2(\sin\lambda_2 - \sin\lambda_1)$. Dividing by the total area of the hemisphere, we derive the fraction f of air in the meteorological northern hemisphere that is transferred to the southern hemisphere over the course of one year:

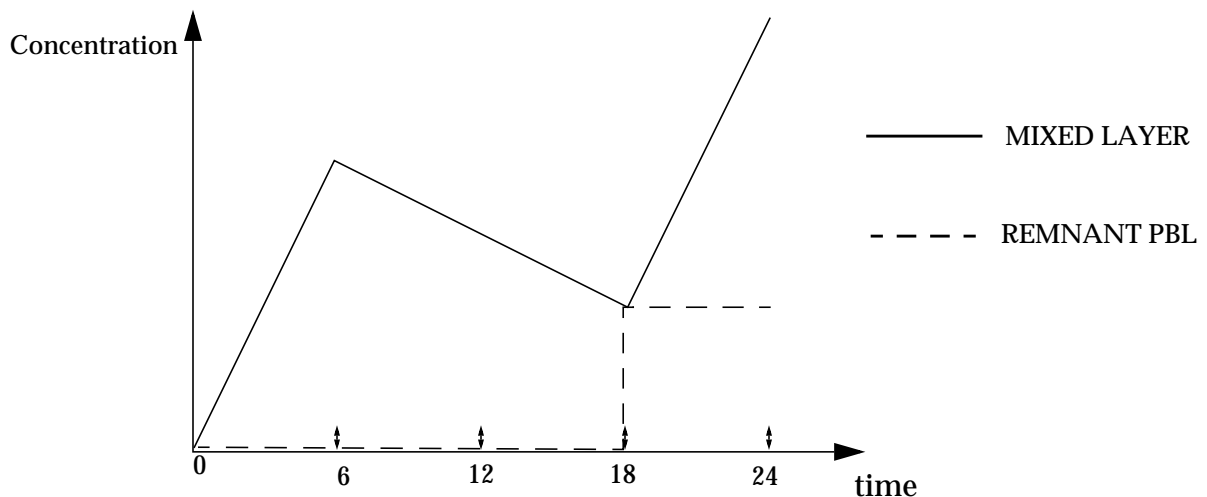
$$f = \frac{m[\lambda_1, \lambda_2]}{m\left[0, \frac{\pi}{2}\right]} = \sin\lambda_2 - \sin\lambda_1 = 0.26$$

This fraction corresponds to a time scale $1/0.26 = 3.9$ years for interhemispheric exchange, much longer than the observed time scale of 1 year. Seasonal motion in the mean latitude of the ITCZ is thus only a minor (though not totally negligible) contributor to interhemispheric exchange.

4. 4 A simple boundary layer model

1. A persistent subsidence inversion caps the PBL at 1.5 km altitude. At night, cooling of the surface produces a second inversion close to the surface; a shallow mixed layer still persists because of wind-induced turbulence. In the daytime, heating of the surface gradually erodes the nighttime inversion and the mixed layer deepens as the day progresses. At sunset, surface cooling causes the mixed layer to collapse rapidly. The greatest weakness of this model is the assumption of a well-mixed remnant PBL (in fact, the remnant PBL is stable and would not be well mixed).

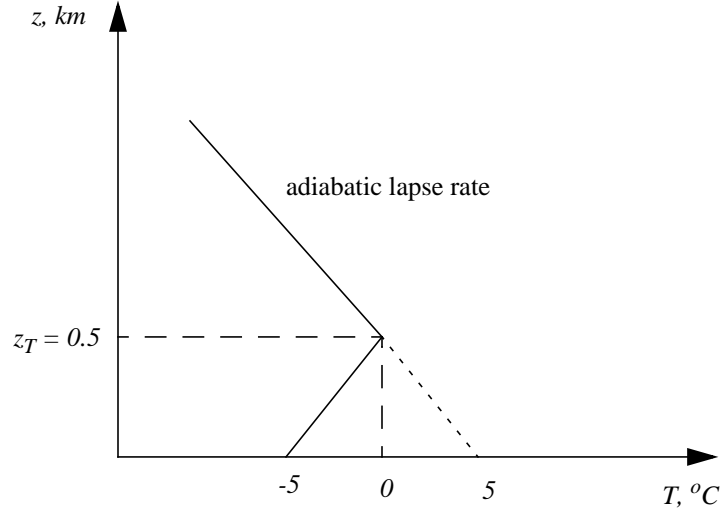
2. From midnight to 6 a.m., the concentration of X increases linearly with time in the mixed layer while the concentration in the remnant PBL remains zero. During daytime from 6 a.m. to 6 p.m., the linear rise in the mixing depth causes dilution of the mixed layer by entrainment of air from the remnant PBL containing zero concentration of X. The mixed layer at 6 p.m. is about 6 times deeper than it was at 6 a.m., while the total amount of X in the mixed layer is only 3 times as much; therefore the concentration of X at 6 p.m. is half of what it was at 6 a.m.. The concentration of X in the remnant PBL remains zero throughout the day because there is no transfer of air from the mixed layer to the remnant PBL. After 6 p.m., the mixed layer collapses and air from the mixed layer is incorporated into the remnant PBL; the concentration in the mixed layer does not change but the remnant PBL now acquires the concentration of the mixed layer. From 6 p.m. to midnight the concentration of X in the mixed layer increases linearly anew while the concentration in the remnant PBL remains constant.



4. 5 Breaking a nighttime inversion

1. Ventilation of the valley requires the establishment of an adiabatic lapse rate $-dT/dz = 10 \text{ K km}^{-1}$ in the lower atmosphere affected by the inversion ($0 < z < z_T = 0.5 \text{ km}$). The corresponding minimum temperature rise is shown as the dotted line in the Figure and is given by

$$\Delta T(z) = a(z_T - z) \quad a = 20 \text{ K km}^{-1}$$



2. Consider an atmospheric column $[0, z_T]$ of unit surface area. The heat input Q to this column necessary to achieve $\Delta T(z)$ is

$$Q = \rho C_p \int_0^{z_T} \Delta T(z) dz$$

where we have integrated over the column $[0, z_T]$ the heating necessary for each column element of thickness dz (mass ρdz). Replacing the expression for $\Delta T(z)$ given above we obtain

$$Q = \rho C_p \int_0^{z_T} a(z_T - z) dz = \frac{\rho C_p a z_T^2}{2}$$

Substituting numerical values (SI units, to be safe!) $\rho = 1 \text{ kg m}^{-3}$, $C_p = 1 \times 10^3 \text{ J kg}^{-1} \text{ } ^\circ\text{K}^{-1}$, $a = 2 \times 10^{-2} \text{ K m}^{-1}$, $z_T = 500 \text{ m}$, we obtain $Q = 2.5 \times 10^6 \text{ J m}^{-2}$.

3. Starting from dawn (t_0), the sun begins to heat the surface. Over a time dt the input of heat is $dQ = F dt$. The valley will be ventilated at the time t_1 when the accumulated heat has reached the value Q derived in question 2:

$$Q = \int_{t_0}^{t_1} F dt$$

Replacing the sinusoidal function $F(t)$ given in the problem, and introducing $t_{noon} = 12 \text{ p.m.}$ and $\Delta t = 24$

hours to stick with symbolic notation throughout:

$$Q = F_{max} \int_{t_0}^{t_1} \cos \frac{2\pi(t - t_{noon})}{\Delta t} dt = F_{max} \frac{\Delta t}{2\pi} \left[\sin \frac{2\pi(t_1 - t_{noon})}{\Delta t} - \sin \frac{2\pi(t_0 - t_{noon})}{\Delta t} \right]$$

so that

$$t_1 = t_{noon} + \frac{\Delta t}{2\pi} \operatorname{asin} \left[\frac{2\pi Q}{F_{max} \Delta t} + \sin \frac{2\pi(t_0 - t_{noon})}{\Delta t} \right]$$

Substituting numerical values we obtain $t_1 = 10:30$ a.m.

4.6 Wet convection

1. Identify stable and unstable regions in the profile.

AB: $-dT/dz = 10 \text{ }^\circ\text{K/km} \geq \Gamma \Rightarrow$ unstable atmosphere

BC: $-dT/dz = 7.5 \text{ }^\circ\text{K/km} < \Gamma \Rightarrow$ stable atmosphere

CD: $-dT/dz = 0 \ll \Gamma \Rightarrow$ very stable atmosphere

2. Cloud formation releases heat by condensation of water vapor, making the parcel more buoyant and facilitating its further rise. For a wet adiabatic lapse rate $\Gamma_W = 6 \text{ K km}^{-1}$ the region BC is conditionally unstable so that cloudy air parcels continue rising up to a maximum altitude z_{max} in the region CD where their temperature reaches $T_{CD} = 265 \text{ K}$; at that point, since the surrounding atmosphere is isothermal at 265 K, further ascent is strongly suppressed. The altitude z_{max} is given by

$$-\frac{T_{CD} - T_B}{z_{max} - z_B} = \Gamma_W \Rightarrow z_{max} = z_B + \frac{T_{CD} - T_B}{\Gamma_W}$$

Substituting $z_B = 2 \text{ km}$, $T_{CD} = 265 \text{ K}$, and $T_B = 280 \text{ K}$, we obtain $z_{max} = 4.5 \text{ km}$.

3. Pollutants released at the surface mix up to 2 km altitude in clear sky and up to 4.5 km in cloudy air; cloud formation greatly improves ventilation.

4.7 Scavenging of water in a thunderstorm

The fraction of water vapor removed by precipitation in the updraft is $f = (C_o - C_{top})/C_o$, where C_o and C_{top} are the water vapor mixing ratios at the base and at the top of the updraft, respectively.

Base of updraft: $z = 1 \text{ km}$, $T = 25 \text{ }^\circ\text{C}$, $P_{H_2O,SAT} = 32 \text{ hPa}$, $P = P(0)\exp[-z/H] = 870 \text{ hPa}$; therefore $C_o = 32/870 = 0.037 \text{ mol/mol}$.

Top of updraft: $z = 15 \text{ km}$, $T = 25 - \Gamma_W z = -31 \text{ }^\circ\text{C}$, $P_{H_2O,SAT} = 0.5 \text{ hPa}$, $P = P(0)\exp[-z/H] = 130 \text{ hPa}$; therefore $C_{top} = 0.5/130 = 3.8 \times 10^{-3} \text{ mol/mol}$.

The fraction of water removed by precipitation is $f = 1 - (3.8 \times 10^{-3}/0.037) = 90\%$.

4. 8 Global source of methane

1. Yes, we would expect CH_4 to be well-mixed in the troposphere because the lifetime of CH_4 (9 years) is much longer than the average time for mixing of the troposphere (1-2 years).

2. We write a mass balance equation for CH_4 in the troposphere:

$$\frac{dN}{dt} = E - L_{trop} - S_{TS}$$

where

- N is the total number of moles of CH_4 in the troposphere; $N = C f N_a$ and $dN/dt = f N_a dC/dt$ where $C = 1700$ ppbv is the mixing ratio of CH_4 , $dC/dt = 10$ ppbv yr^{-1} is the growth rate of CH_4 , $N_a = 1.8 \times 10^{20}$ moles is the total number of moles of air in the atmosphere (chapter 2), and $f = 0.85$ is the fraction of that total in the troposphere (taking a 150 hPa tropopause).
- E (moles yr^{-1}) is the global emission rate of CH_4 , which we wish to derive.
- L_{trop} (moles yr^{-1}) is the global loss rate of CH_4 from oxidation in the troposphere; $L_{trop} = N/\tau_{ox}$ where $\tau_{ox} = 9$ years is the lifetime of CH_4 in the troposphere.
- S_{TS} (moles yr^{-1}) is the net flow rate of CH_4 from the troposphere to the stratosphere. For now we assume $S_{TS} = 0$.

Replacing in the mass balance equation we obtain:

$$\begin{aligned} E &= f N_a \frac{dC}{dt} + \frac{f N_a C}{\tau_{ox}} = f N_a \left(\frac{dC}{dt} + \frac{C}{\tau_{ox}} \right) \\ &= 0.85 \times 1.8 \times 10^{20} \left(10 \times 10^{-9} + \frac{1700 \times 10^{-9}}{9} \right) = 3.0 \times 10^{13} \text{ moles yr}^{-1} \end{aligned}$$

3.1 We write a mass balance for CH_4 in the stratosphere, assuming steady state:

$$S_{TS} = L_{strat}$$

where L_{strat} is the loss rate of CH_4 in the stratosphere; $S_{TS} = A F_{TS}$ where A is the surface area of the Earth and F_{TS} is the mean flux of CH_4 across the tropopause. From the eddy diffusion formulation of the turbulent flux, F_{TS} is given by

$$F_{TS} = \left[-K_z n_a \frac{dC}{dz} \right]_{tropopause}$$

and hence

$$L_{strat} = -A \left[K_z n_a \frac{dC}{dz} \right]_{tropopause}$$

Here K_z and dC/dz are not to be evaluated exactly at the tropopause (because of discontinuity in dC/dz) but just above.

3.2 We need to calculate dC/dz in the stratosphere. From

$$C(z) = C(z_t) e^{\left[-\frac{(z-z_t)}{h} \right]}$$

we obtain

$$\frac{dC}{dz} = C(z_t) \left(-\frac{1}{h}\right) e^{\left[-\frac{(z-z_t)}{h}\right]}$$

Just above the tropopause ($z \approx z_t$),

$$\left. \frac{dC}{dz} \right|_{\text{tropopause}} = \frac{-C(z_t)}{h}$$

where $C(z_t) = 1700$ ppbv and $h = 60$ km. We replace into the equation from question 3.1, with the numerical values $K_z = 7 \times 10^{-1} \text{ m}^2 \text{ s}^{-1}$ and $n_a = 5 \times 10^{24} \text{ molecules m}^{-3}$, and including $A = 5.1 \times 10^{14} \text{ m}^2$ for the surface area of the Earth. Note that the resulting L_{strat} is in units of molecules s^{-1} .

$$\begin{aligned} L_{\text{strat}} &= -A \left[K_z n_a \frac{dC}{dz} \right]_{\text{tropopause}} = \frac{AK_z n_a C(z_t)}{h} \\ &= \frac{5.1 \times 10^{14} \times 7 \times 10^{-1} \times 5 \times 10^{24} \times 1700 \times 10^{-9}}{60 \times 10^3} = 5.1 \times 10^{28} \text{ molecules s}^{-1} = 2.7 \times 10^{12} \text{ moles yr}^{-1} \end{aligned}$$

Replacing now $S_{TS} = L_{\text{strat}}$ in the mass balance equation for CH_4 in the troposphere:

$$\frac{dN}{dt} = E - L_{\text{trop}} - L_{\text{strat}}$$

we obtain an improved estimate of E :

$$E = 3.0 \times 10^{13} + 2.7 \times 10^{12} = 3.3 \times 10^{13} \text{ moles yr}^{-1}$$

4.9 Role of molecular diffusion in atmospheric transport

1. We use the Einstein diffusion equation to find the average time Δt needed for a molecule to travel a distance $\Delta x = 1$ m by molecular diffusion:

$$\Delta t = \frac{(\Delta x)^2}{2D} = \frac{(\Delta x)^2 P}{2D_0 P_0} = \frac{(\Delta x)^2}{2D_0} \exp\left[-\frac{z}{H}\right]$$

where we have replaced $D = D_0(P_0/P)$ and the Barometric Law $P = P_0 \exp[-z/H]$; $H = 7.4$ km is the atmospheric scale height. Since molecular diffusion is isotropic, Δx applies to any direction (vertical or horizontal).

From the above equation with $\Delta x = 1$ m and $D_0 = 0.2 \text{ cm}^2 \text{ s}^{-1}$ we find $\Delta t = 6.9$ hours at $z = 0$ km, $\Delta t = 1.8$ hours at $z = 10$ km, $\Delta t = 0.03$ s at $z = 100$ km. We see that molecular diffusion is very slow compared to typical time scales for atmospheric motion in the lowest scale heights of the atmosphere. At 10 km, the molecular diffusion coefficient is $D = 0.8 \text{ cm}^2 \text{ s}^{-1}$; compare to a typical turbulent diffusion coefficient $K_z \sim 10^5 \text{ cm}^2 \text{ s}^{-1}$. At 100 km, molecular diffusion is fast because the air density is low so that the mean free path between collisions is long.

2. For molecular diffusion to be more important than turbulent diffusion, we must have

$$D > K_z \Rightarrow D_0 \exp\left[\frac{z}{H}\right] > K_z \Rightarrow z > H \ln \frac{K_z}{D_0} = 7.4 \ln \frac{1 \times 10^5}{0.2} = 97 \text{ km}$$

Molecular diffusion becomes the dominant mechanism for vertical transport above 100 km.

4. 10 Vertical transport near the surface

The vertical flux of the species is given by

$$F = -K_z n_a \frac{dC}{dz} = -\alpha z n_a \frac{dC}{dz}$$

from which we obtain a relationship between C and z ,

$$dC = -\frac{F}{\alpha n_a} \frac{dz}{z}$$

Since the only sink for the species is reaction at the Earth's surface, F at steady state is independent of z (the vertical flux is conserved). In addition, near the surface we can neglect vertical changes in the air density n_a . Integration of the above equation between any two altitudes z_1 and z_2 yields therefore a logarithmic increase of C with altitude:

$$C(z_2) = C(z_1) - \frac{F}{\alpha n_a} (\ln z_2 - \ln z_1)$$

Note that C increases with altitude in the above equation because F is negative (it is directed toward the surface).

SOLUTIONS TO PROBLEMS, CHAPTER 5

5.1 Turbulent diffusion coefficient

1. The one-dimensional continuity equation includes terms from vertical transport (parameterized by a turbulent diffusion coefficient) and chemical loss. Emission of ^{222}Rn at the surface is a boundary condition and does not enter into the equation.

$$\frac{\partial n}{\partial t} = \frac{\partial}{\partial z} \left[KN \frac{\partial C}{\partial z} \right] - kn$$

2. In the above equation we replace $C(z) = C(0)\exp(-z/h)$, $\partial n / \partial t = 0$ (steady state), and

$$n = NC = N(0)C(0)\exp\left[-\left(\frac{1}{H} + \frac{1}{h}\right)z\right]$$

where N is the air density. The result is

$$0 = \frac{\partial}{\partial z} \left[-\frac{K}{h} N_0 C_0 e^{-z\left(\frac{1}{H} + \frac{1}{h}\right)} \right] - k N_0 C_0 e^{-z\left(\frac{1}{H} + \frac{1}{h}\right)}$$

which yields upon further derivation

$$\frac{K}{h} \left(\frac{1}{H} + \frac{1}{h} \right) = k$$

Rearranging,

$$K = \frac{kh}{\frac{1}{H} + \frac{1}{h}} = 1.3 \times 10^5 \text{ cm}^2 \text{ s}^{-1}$$

3. The emission flux E of ^{222}Rn from the soil is given by the turbulent diffusion flux at $z = 0$:

$$E = -Kn_a(0) \frac{\partial C}{\partial z} \Big|_{z=0}$$

Replacing $C(z) = C(0)\exp(-z/h)$, we obtain

$$E = \frac{Kn_a(0)}{h} C(0) = \frac{Kn(0)}{h} = \frac{1.3 \times 10^5 \times 2}{3 \times 10^5} = 0.87 \text{ atoms cm}^{-2} \text{ s}^{-1}$$

4. By rearranging the solution to question (2) we obtain a quadratic equation for h for which the solution is

$$h = \frac{\frac{K}{kH} \pm \sqrt{\left(\frac{K}{kH}\right)^2 + \frac{4K}{k}}}{2}$$

In this manner we can derive h for any gas of known k , assuming K to be constant in the atmosphere.

The residence time of water vapor in the atmosphere is 13 days. Assuming the loss of water by precipitation to be a continuous first-order process, the corresponding loss rate constant is $k = 1/(13 \text{ days}) = 8.9 \times 10^{-7} \text{ s}^{-1}$. Substituting in the above equation gives $h = 5.0 \text{ km}$ for water vapor.

SOLUTIONS TO PROBLEMS, CHAPTER 6

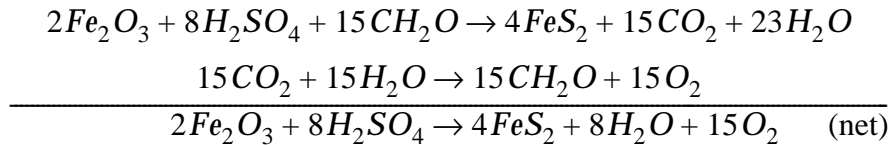
6. 1 Short questions on the oxygen cycle

1. The statement is wrong. The tropical rainforests are actually not net sources of oxygen because the O_2 generated during the production of organic carbon by photosynthesis is eventually consumed by oxidation of this organic carbon back to CO_2 when the plant dies.

1. The developer's reasoning is that cutting down mature trees and sealing them against oxidation will prevent the O_2 generated during the growth of the tree to be consumed by oxidizing organic carbon when the tree decays. In this manner O_2 levels will increase. The flaw in the reasoning is that the increase in O_2 will be limited by the amount of atmospheric CO_2 available for photosynthesis. Since atmospheric CO_2 is less than 0.2% of atmospheric O_2 , we will run out of CO_2 before having produced any significant increase in O_2 . So the plan would not work.

3. The CO_2 produced in the bacterial reaction will eventually bubble out of the ocean and be consumed by photosynthesis, generating O_2 . Another (equivalent) perspective is that the reaction oxidizes organic carbon to CO_2 by using Fe_2O_3 and H_2SO_4 as oxygen sources, i.e., without consuming O_2 . In this manner the O_2 previously generated in the production of the organic carbon is not consumed in the eventual oxidation of this organic carbon, resulting in a net O_2 source.

By summing the reaction and the eventual photosynthesis of the CO_2 produced,



we see that the net effect of the reaction is to convert Fe_2O_3 and H_2SO_4 to FeS_2 , H_2O , and O_2 . The Fe_2O_3 and H_2SO_4 originate in turn from oxidation of FeS_2 in the lithosphere by the reverse reaction, closing the O_2 cycle. The bacterial reaction is therefore part of the atmosphere-lithosphere cycle of oxygen.

4. Most H atoms in the atmosphere are present as H_2O . Photolysis of H_2O frees H atoms. When these H atoms escape to space, they leave behind the O atoms which are then eventually converted to O_2 (the dominant form of oxygen in the atmosphere). If the H atoms do not escape to space, they recombine with O atoms to regenerate H_2O and there is no net production of O_2 .

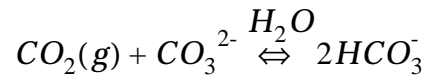
The H atom escape rate is $5.4 \times 10^7 \text{ kg yr}^{-1} = 5.4 \times 10^{10} \text{ moles yr}^{-1}$. Essentially all of the escaping H originates from breakdown of the H_2O molecule, and the resulting net source of O atoms to the atmosphere is $2.7 \times 10^{10} \text{ moles yr}^{-1} = 4.3 \times 10^8 \text{ kg yr}^{-1}$. Assuming that the rate has remained constant since the beginning of the Earth 4.5×10^9 years ago, the total amount of O_2 produced by this mechanism is $1.9 \times 10^{18} \text{ kg}$. In comparison, the organic carbon inventory in sediments indicates that photosynthesis of primeval CO_2 in the early Earth must have provided an O_2 source of $3.2 \times 10^{19} \text{ kg}$ (see exercise in chapter 6). Photosynthesis of primeval CO_2 thus played a more important role than photolysis of H_2O as an original source of O_2 to the atmosphere.

5. The source of O_2 from photosynthesis is limited to spring and summer, while the sink of O_2 from oxidation of dead biomass is more evenly spread over the year. We expect therefore a summer peak for O_2 concentrations. The seasonal variation of O_2 is the reverse of that of CO_2 ,

since the source of O_2 is a sink of CO_2 and vice versa. Considering that there is a 1:1 $O_2:CO_2$ stoichiometry in these sources and sinks, the amplitudes of the seasonal cycles should be the same for both O_2 and CO_2 . The time series of CO_2 at Mauna Loa, Hawaii, shows about a 3 ppbv seasonal amplitude (Fig 6-7 of sourcebook) and the same seasonal amplitude should apply to O_2 .

6. 2 Short questions on the carbon cycle

1. Uptake of CO_2 by the oceans follows the stoichiometry



Removing CO_3^{2-} by coral formation will push the equilibrium to the left, releasing CO_2 to the atmosphere. It may seem counterintuitive that by stocking carbon in the oceans through coral formation one would increase CO_2 ; the key is that coral formation removes alkalinity (CO_3^{2-}) from the ocean.

2. The residence time of air in the stratosphere is 1-2 years, so that CO_2 concentrations in the stratosphere represent those found in the troposphere 1-2 years before. The growth rate of CO_2 in the troposphere is 1-2 ppmv yr⁻¹, and the time lag for transfer of air from the troposphere to the stratosphere thus results in a 1-2 ppmv difference in concentrations between the two reservoirs.

3. No, because food production involves photosynthesis by crops which is a source of O_2 and balances exactly the source of CO_2 when this food is ingested.

4. Melting of the polar ice caps freshens the water of the polar surface oceans, making it lighter and hence less likely to sink to the deep ocean. The decrease in deep water formation slows down the uptake of CO_2 by the ocean, and the resulting increase of CO_2 in the atmosphere represents a positive feedback to global warming.

5. The statement is not intrinsically correct although it may have some political truth. Planting trees does reduce the stock of carbon present in the atmosphere as CO_2 . Note that the amount of organic carbon in the biosphere is larger than the amount of CO_2 in the atmosphere, so that growing the biosphere does give us leverage for decreasing CO_2 . Although the organic carbon in a tree returns to the atmosphere when the tree dies ("in less than a century"), as long as the forest is maintained a new tree will grow in its place. The catch is that a plan to reduce CO_2 by growing the biosphere requires a long-term commitment to the preservation of the stock of organic carbon in the new ecosystems. If these stocks are allowed to return to the atmosphere as CO_2 (as for example if the dying trees are not replaced, or if the forest is cut or burned to return to its original use) then the gains will be lost.

6. 3 Atmospheric residence time of helium

1. Helium is sufficiently light to overcome Earth's gravity and escape to outer space.

2. The mass m_{Ar} of argon in the present-day atmosphere is:

$$m_{Ar} = C_{Ar} \frac{M_{Ar}}{M_{air}} m_{air} = 9340 \times 10^{-6} \times \frac{40}{29} \times 5.2 \times 10^{18} = 6.7 \times 10^{16} \text{ kg}$$

Since there is no sink for argon in the atmosphere, the mean source rate \bar{P}_{Ar} over the Earth's history $\Delta t = 4.5 \times 10^9$ years is

$$\bar{P}_{Ar} = \frac{m_{Ar}}{\Delta t} = 1.5 \times 10^7 \text{ kg yr}^{-1}$$

3. The production rate of argon at any given time in Earth's history depends on the remaining mass m_K of ^{40}K in the Earth's interior:

$$P_{Ar}(t) = km_K(t)$$

This mass m_K has been decreasing exponentially since the formation of the Earth:

$$m_K(t) = m_K(0)e^{-kt}$$

so that

$$P_{Ar}(t) = km_K(0)e^{-kt}$$

The mean value of P_{Ar} over time Δt is then given by

$$\bar{P}_{Ar} = \frac{1}{\Delta t} \int_0^{\Delta t} P_{Ar}(t) dt = \frac{1}{\Delta t} \int_0^{\Delta t} km_K(0)e^{-kt} dt = \frac{km_K(0)}{\Delta t} \int_0^{\Delta t} e^{-kt} dt = \frac{m_K(0)}{\Delta t} (1 - e^{-k\Delta t})$$

and the value of P_{Ar} at time Δt is given by

$$P_{Ar}(\Delta t) = km_K(0)e^{-k\Delta t}$$

Taking the ratio between the two:

$$\frac{P_{Ar}(\Delta t)}{\bar{P}_{Ar}} = \frac{k\Delta t}{\exp(k\Delta t) - 1} = 0.23$$

which is the desired result.

4. From the previous equation, the present-day source of argon is

$$P_{Ar}(\Delta t) = 0.23 \bar{P}_{Ar} = 0.23 \times 1.5 \times 10^7 = 3.5 \times 10^6 \text{ kg yr}^{-1}$$

and, since we are told that the source of helium is the same,

$$P_{He}(\Delta t) = P_{Ar}(\Delta t) = 3.5 \times 10^6 \text{ kg yr}^{-1}$$

The present-day mass $m_{He}(\Delta t)$ of helium in the atmosphere can be derived from the observed mixing ratio of 5.2 ppmv:

$$m_{He} = C_{He} \frac{M_{He}}{M_{air}} m_{air} = 5.2 \times 10^{-6} \times \frac{4}{29} \times 5.2 \times 10^{18} = 3.7 \times 10^{12} \text{ kg}$$

Assuming steady state for helium, the atmospheric lifetime of He against escape to outer space is

$$\tau_{He} = \frac{m_{He}(\Delta t)}{P_{He}(\Delta t)} = \frac{3.7 \times 10^{12}}{3.5 \times 10^6} = 1.1 \text{ million years}$$

6. 4 Methyl bromide

1.1 The lifetime of CH_3Br against oxidation in the atmosphere is sufficiently long (2.0 years) that its atmospheric mixing ratio C can be assumed uniform. We can relate C to the sea-level values of the partial pressure $P_{\text{CH}_3\text{Br}}$ and the total atmospheric pressure P_a :

$$C = \frac{P_{\text{CH}_3\text{Br}}}{P_a}$$

The total number of moles of CH_3Br in the atmosphere is then

$$n_{\text{atm}} = CN_a = \frac{P_{\text{CH}_3\text{Br}}}{P_a} N_a$$

where $N_a = 1.8 \times 10^{20}$ moles is the total number of moles of air in the atmosphere. The total number of moles of CH_3Br in the oceanic mixed layer can be similarly related to the sea-level partial pressure of CH_3Br :

$$n_{\text{ocean}} = V[\text{CH}_3\text{Br}(\text{aq})] = VK_H P_{\text{CH}_3\text{Br}}$$

where $V = 3.6 \times 10^{19}$ l is the volume of the oceanic mixed layers. Therefore,

$$\frac{n_{\text{ocean}}}{n_{\text{atm}}} = \frac{VK_H P_a}{N_a} = \frac{3.6 \times 10^{19} \cdot 0.11 \cdot 1}{1.8 \times 10^{20}} = 0.022$$

There is 45 times more CH_3Br in the atmosphere than in the oceanic mixed layer.

1.2 The atmospheric lifetime τ_{hyd} of CH_3Br against hydrolysis in the ocean is defined as

$$\tau_{\text{hyd}} = \frac{n_{\text{atm}}}{k_o n_{\text{ocean}}}$$

Note that we cannot take $n_{\text{atm}}/n_{\text{ocean}}$ from the answer to question 1.1 because loss by hydrolysis ($k_o > k_2$) reduces n_{ocean} below equilibrium with the gas phase (if there were no hydrolysis then steady state would give us $n_{\text{ocean}}/n_{\text{atm}} = k_1/k_2 = 0.023$, which is the equilibrium value from the previous question). Accounting for hydrolysis, we write the steady state equation for $\text{CH}_3\text{Br}(\text{aq})$:

$$k_1 n_{\text{atm}} = (k_o + k_2) n_{\text{ocean}}$$

and replace in the above equation for τ_{hyd} :

$$\tau_{\text{hyd}} = \frac{k_o + k_2}{k_o k_1} = 3.3 \text{ years}$$

1.3 The lifetime of $\text{CH}_3\text{Br}(\text{aq})$ against hydrolysis is $1/k_o = 0.025$ years, which is too short to allow significant transfer to the deep ocean (the residence time of water in the oceanic mixed layer is 20 years). Therefore the deep ocean does not represent an important reservoir for CH_3Br , in contrast to CO_2 .

1.4 The atmospheric lifetime τ of CH_3Br reflects the contributions of sinks from atmospheric oxidation ($\tau_{\text{ox}} = 2.0$ years) and hydrolysis in the ocean ($\tau_{\text{hyd}} = 3.3$ years) operating in parallel:

$$\tau = (\tau_{\text{ox}}^{-1} + \tau_{\text{hyd}}^{-1})^{-1} = 1.2 \text{ years}$$

1.5 Methylbromide emitted to the troposphere can be removed by the processes described above (rate constant $k' = 1/\tau$) or by transport to the stratosphere (rate constant k_{TS}). The fraction f transported to the stratosphere is therefore

$$f = \frac{k_{TS}}{k' + k_{TS}} = \frac{0.14}{0.83 + 0.14} = 0.14$$

14% of the emitted CH_3Br enters the stratosphere and is therefore active in depletion of the stratospheric ozone layer.

2.1 We write the steady-state equation for m_S , assuming no emissions in the southern hemisphere:

$$km_N = (k + k')m_S \Rightarrow R = \frac{m_N}{m_S} = 1 + \frac{k'}{k} = 1 + \frac{0.8}{0.9} = 1.9$$

2.2 Let A represent the anthropogenic source (assumed to be located exclusively in the northern hemisphere) and B represent the biogenic source (distributed equally between the two hemispheres). We write the steady-state equations for the total atmospheric mass $m = m_N + m_S$ of CH_3Br in the atmosphere, and for m_S separately (note that a third equation for m_N separately would be redundant):

$$A + B = k'm \quad (1)$$

$$\frac{B}{2} + km_N = (k + k')m_S \quad (2)$$

We now divide the second equation by m_S , and replace $R = m_N/m_S$ and $m_S = m/(1+R)$:

$$\frac{B(1+R)}{2m} + kR = k + k' \Rightarrow B = \frac{2m}{1+R}(k + k' - kR) \quad (3)$$

The biogenic fraction f of the global source is

$$f = \frac{B}{A+B} \quad (4)$$

Replacing (1) and (3) into (4):

$$f = \frac{\frac{2m}{1+R}(k + k' - kR)}{k'm} = \frac{2(k + k' - kR)}{(1+R)k'}$$

Substituting the observed value $R = 1.3$, and numerical values for k and k' , we obtain $f = 0.58$. Thus 58% of the global source of CH_3Br must be biogenic.

2.3 There is no contradiction. Methyl bromide is produced biogenically in the oceans; a fraction is lost by hydrolysis in the ocean while the rest escapes to the atmosphere. The atmospheric fraction may be oxidized in the atmosphere or eventually return to the ocean and get hydrolyzed. Hydrolysis in the

oceans also acts as a sink for anthropogenic CH_3Br .

6. 5 The nitrogen cycle

1. Residence time $\tau = (\text{inventory})/(\text{flow out})$. Inventories are in Tg N, flows are in Tg N yr^{-1} ; the resulting values for τ are in units of years.

Atmospheric N_2 : $\tau = 3.9 \times 10^9 / (80 + 160 + 30 + 20) = 13$ million years

Atmospheric fixed N: $\tau = 3 / (80 + 30) = 2.7 \times 10^{-2}$ years = 10 days

Land biota: $\tau = 1.0 \times 10^4 / 2500 = 4$ years

Land soil: $\tau = 7 \times 10^4 / (2300 + 130 + 80 + 40) = 27$ years

Ocean biota: $\tau = 1000 / (1600 + 100) = 0.59$ years = 7 months

Deep ocean: $\tau = 8 \times 10^5 / (1600 + 10) = 500$ years

Lithosphere: $\tau = 2 \times 10^9 / 10 = 2 \times 10^8$ years = 200 million years.

2. Land reservoir = Land biota + Land soil :

inventory = $1 \times 10^4 + 7 \times 10^4 = 8 \times 10^4$ Tg N

flow out = $130 + 80 + 40 = 250$ Tg N yr^{-1}

$\tau = 8 \times 10^4 / 250 = 320$ years

The residence time in the combined land reservoir is much longer than the residence time in either of the biota or soil reservoir because the rate of cycling between the land biota and land soil is much faster than the loss out of the combined reservoir.

3. When we add nitrogen to the land biota, it reaches a dynamic equilibrium with the land soil reservoir on a time scale $\tau_{\text{land biota}} = 4$ years, which is much shorter than the 100-year time scale we are asked to consider. By contrast, loss out of the combined land reservoir ($\tau = 320$ years) is slow relative to the 100-year time scale; we can therefore consider that the added nitrogen has accumulated in the land reservoir over the past 100 years. The added nitrogen includes contributions from industrial fertilizer, nitrogen-fixing crops, and fossil fuel combustion. All of the industrial fertilizer and nitrogen-fixing crops (130 Tg N yr^{-1}) are applied to the land reservoir. However, only a fraction f of the 25 Tg N yr^{-1} fixed by fossil fuel combustion is deposited to land; the rest is deposited to the oceans. From the flow rates given in the diagram this fraction is $f = 80 / (80 + 30) = 0.7$. The accumulation of N in the land reservoir is therefore $130 + (0.7 \times 25) = 150$ Tg N yr^{-1} , amounting to 1.5×10^4 Tg N over 100 years.

The present-day inventory of the land reservoir is 8×10^4 Tg N; from the above we conclude that the inventory 100 years ago was $8 - 1.5 = 6.5 \times 10^4$ Tg N. There has been a 23% increase in the size of the land reservoir over the past 100 years. Because of the rapid cycling between the land biota and the land soil, this percentage increase may be expected to apply to both biota and soil. This is a substantial global fertilization effect.

We apply the same reasoning to the ocean biota. On a time scale of 100 years, the ocean biota and deep ocean reservoirs are in dynamic equilibrium; the residence time of N in the sum of these two reservoirs (let's call it the "ocean reservoir") is $8 \times 10^5 / 100 = 8,000$ years, much longer than our 100-year horizon. Over the past 100 years, fossil fuel combustion has added $100 \times (0.3 \times 25) = 750$ Tg N to the ocean reservoir; this amounts to only $750 / 8 \times 10^5 = 0.1\%$ of the N inventory in that reservoir.

We conclude that there is potential for significant global fertilization of the land biosphere by human

activity but not of the ocean biosphere.

6. 6 Ocean pH

From the formulations of the equilibrium constants:

$$K_H = \frac{[CO_2 \cdot H_2O]}{P_{CO_2}}$$

$$K_1 = \frac{[HCO_3^-][H^+]}{[CO_2 \cdot H_2O]}$$

$$K_2 = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]}$$

$$K_S = [Ca^{2+}][CO_3^{2-}]$$

we can express $[H^+]$ in terms of the input data to the problem:

$$[H^+] = \left[\frac{K_H K_1 K_2}{K_S} [Ca^{2+}] P_{CO_2} \right]^{\frac{1}{2}}$$

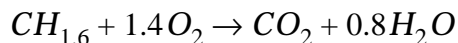
Substituting numerical values we obtain an ocean pH = 8.1.

6. 7 Cycling of CO₂ with the terrestrial biosphere

1. The total mass of carbon in the terrestrial vegetation reservoir is 730 Pg C. The total loss rate out of this reservoir is 62 Pg C yr⁻¹. Dividing the total mass by total loss rate, we find a lifetime of 12 years.
2. By comparing the different fluxes out of the litter reservoir, we see that the dominant fate of carbon in the litter is export to the atmosphere. Only 3/54 = 6% is incorporated into the soil.
3. Atmospheric CO₂ would decrease if the source from microbial activity decreases, because more carbon could then be stored in the soil reservoir (which is larger than the atmospheric reservoir).

6. 8 Sink of atmospheric CO₂ deduced from changes in atmospheric O₂

1.1 The stoichiometric representation of fossil fuel combustion is



Therefore, 1.4 moles of O₂ are consumed per mole of CO₂ emitted by fossil fuel combustion.

1.2 The stoichiometric representation of photosynthesis given in the chapter shows that one mole of O₂ is produced per mole of CO₂ taken up by the biosphere.

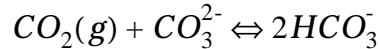
1.3 Oxygen is not involved in the dissolution and subsequent dissociation of CO_2 in the ocean. There is no O_2 produced or consumed when atmospheric CO_2 is removed by this process.

2.1 Fossil fuel combustion over the 3-year period amounted to $3 \times 6.3 \times 10^{12} = 18.9 \times 10^{12}$ kg C = 1.6×10^{15} moles CO_2 . The total number of moles of air is 1.8×10^{20} moles. Fossil fuel combustion would therefore have caused a 8.9 ppmv increase in CO_2 and a $1.4 \times 8.9 = 12.4$ ppmv decrease in O_2 .

2.2 The observed decrease of O_2 is 8.8 ppmv, less than the 12.4 ppmv predicted from fossil fuel combustion alone. The difference of 3.6 ppmv can be explained by uptake of CO_2 by the biosphere. If we correct the predicted CO_2 increase from fossil fuel combustion by this uptake, we find a net increase of CO_2 of $8.9 - 3.6 = 5.3$ ppmv. However, the observations show a CO_2 increase of 3.2 ppmv. This means that $5.3 - 3.2 = 2.1$ ppmv of CO_2 must have dissolved into the oceans. Therefore, of the 8.9 ppmv CO_2 injected into the atmosphere by fossil fuel combustion, (a) 3.6 ppmv or 40% were taken up by the biosphere; (b) 2.1 ppmv or 24% dissolved in the ocean; (c) and 3.2 ppmv or 36% accumulated in the atmosphere.

5. Fossil fuel CO_2 neutralization by marine CaCO_3

1. Dissolution of CaCO_3 provides a source of base (CO_3^{2-}) to the ocean, facilitating uptake of $\text{CO}_2(\text{g})$ following the equilibrium

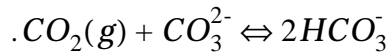


2. Equilibrium between CaCO_3 on the ocean floor and CO_3^{2-} in the ocean is defined by

$$[\text{Ca}^{2+}][\text{CO}_3^{2-}] = K_s$$

If $[\text{Ca}^{2+}]$ is constant then $[\text{CO}_3^{2-}]$ must also remain constant between the preindustrial and final states, since equilibrium is satisfied in both states.

3. The equilibrium



has an equilibrium constant

$$\frac{[\text{HCO}_3^-]^2}{P_{\text{CO}_2}[\text{CO}_3^{2-}]} = \frac{K_H K_1}{K_2}$$

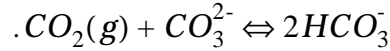
Therefore,

$$\left\{ \frac{[\text{HCO}_3^-]^2}{P_{\text{CO}_2}[\text{CO}_3^{2-}]} \right\}_{\text{preindustrial}} = \left\{ \frac{[\text{HCO}_3^-]^2}{P_{\text{CO}_2}[\text{CO}_3^{2-}]} \right\}_{\text{final}}$$

and since $[\text{CO}_3^{2-}]_{\text{final}} = [\text{CO}_3^{2-}]_{\text{preindustrial}}$, we have the desired relationship:

$$\frac{P_{CO_2, \text{final}}}{P_{CO_2, \text{preindustrial}}} = \left(\frac{[HCO_3^-]_{\text{final}}}{[HCO_3^-]_{\text{preindustrial}}} \right)^2$$

4. $CO_2(g)$ enters the ocean by



which consumes CO_3^{2-} from the ocean. Since the ocean CO_3^{2-} concentration in the final state is the same as in the initial state, CO_3^{2-} must be replenished by dissolution of $CaCO_3$ from the ocean floor. From the above equilibrium, we see that every molecule of $CO_2(g)$ entering the ocean adds two HCO_3^- molecules to the ocean (one originating from the dissolution of $CO_2(g)$, the other one from dissolution of $CaCO_3$). If we emit to the atmosphere all the identified fossil fuel reserves (5×10^{18} g C), and all of this carbon enters the ocean, the mass of HCO_3^- in the ocean will increase by 10×10^{18} g C.

5. Substituting the above result in the equation of question 3:

$$\frac{P_{CO_2, \text{final}}}{P_{CO_2, \text{preindustrial}}} = \left(\frac{[HCO_3^-]_{\text{final}}}{[HCO_3^-]_{\text{preindustrial}}} \right)^2 = \left(\frac{38 + 10}{38} \right)^2 = 1.60$$

With $P_{CO_2, \text{preindustrial}} = 280$ ppmv we find $P_{CO_2, \text{final}} = 450$ ppmv. The difference, 170 ppmv, corresponds to a carbon mass of $170 \times 10^{-6} \times 1.8 \times 10^{20} \times 12 = 3.6 \times 10^{17}$ g C remaining in the atmosphere. Comparing to the total fossil fuel carbon emitted (5×10^{18} g C), we conclude that $3.6 \times 10^{17} / 5 \times 10^{18} = 7\%$ of the emitted CO_2 remains in the atmosphere. This is substantially less than the 28% fraction calculated without accounting for $CaCO_3$ dissolution!

SOLUTIONS TO PROBLEMS, CHAPTER 7

7. 1 Climate response to changes in ozone

1. Ozone is a major source of heat in the stratosphere. Removing all ozone above 30 km will therefore result in a large stratospheric cooling. It will also allow more UV radiation to penetrate to the troposphere, resulting in tropospheric warming.

2. Ozone is a far more effective greenhouse gas in the upper troposphere than in the lower troposphere because of the decrease of temperature with altitude. Radiation emitted by the Earth's surface and absorbed by ozone in the upper troposphere is reemitted at a much lower temperature, reducing the radiation flux escaping to space and therefore warming the Earth's surface. In contrast, radiation absorbed by ozone near the surface is reemitted at nearly the same temperature as the surface, so that the greenhouse effect is minimal.

7. 2 Interpretation of the terrestrial radiation spectrum

1. The radiation flux measured in the atmospheric window (8-12 μm , or 800-1250 cm^{-1}), where absorption by the atmosphere is minimal, represents blackbody emission from the Earth's surface. The corresponding surface temperatures are 320 K (Sahara), 280 K (Mediterranean), and 180 K (Antarctica).

2. The dips at 600-700 cm^{-1} (14-16 μm) and 1000-1050 cm^{-1} (9.5-10 μm) in the emission spectra for the Sahara and Mediterranean Sea are due to atmospheric absorption and reemission by CO_2 and O_3 , respectively. The corresponding temperatures of 220 K (600-700 cm^{-1}) and 250-280 K (1000-1050 cm^{-1}) represent the "tops" of the atmospheric columns, roughly the tropopause for CO_2 and the upper stratosphere for O_3 . These dips become bumps in the emission spectrum over Antarctica because the surface there is colder than the atmosphere overhead.

7. 3 Jupiter and Mars

1.1 Calculate the effective temperature T_J of Jupiter assuming that the Sun is the only energy source:

$$T_J = \left[\frac{F_S(1-A)}{4\sigma} \right]^{\frac{1}{4}} = \left[\frac{\sigma T_S^4 \left(\frac{R_S}{d} \right)^2 (1-A)}{4\sigma} \right]^{\frac{1}{4}} = T_S \left(\frac{R_S}{d} \right)^{\frac{1}{2}} \left(\frac{1-A}{4} \right)^{\frac{1}{4}}$$

Substituting numerical values we find $T_J = 89 \text{ K}$.

1.3 Let H be the internal energy source per unit area of Jupiter's surface. We write an energy balance equation for the planet:

$$H + \frac{F_S(1-A)}{4} = \sigma T_J^4$$

From question 1.1, $F_S(1-A)/4 = \sigma T_{J,o}^4$ where $T_{J,o} = 89 \text{ K}$ is the effective temperature of Jupiter computed without the internal energy source. Therefore,

$$H = \sigma(T_J^4 - T_{J,o}^4)$$

The ratio R of the internal energy source to the energy received from the Sun is

$$R = \frac{H}{\frac{F_S(1-A)}{4}} = \frac{T_J^4 - T_{J,o}^4}{T_{J,o}^4} = \left(\frac{T_J}{T_{J,o}}\right)^4 - 1 = \left(\frac{134}{89}\right)^4 - 1 = 4.1$$

Jupiter's temperature is therefore maintained principally by internal sources of heat.

2.1 Effective temperature of Mars:

$$T_M = T_S \left(\frac{R_S}{d}\right)^{\frac{1}{2}} \left(\frac{1-A}{4}\right)^{\frac{1}{4}} = 218 \text{ K}$$

2.2 The observed surface temperature of Mars, 220 K, is only 2 K higher than the effective temperature. We conclude that the atmosphere on Mars provides only a small greenhouse effect, much smaller than on Earth where the difference between surface and effective temperatures is $288 - 255 = 33 \text{ K}$.

7.4 The “faint Sun” problem

1. From our simple greenhouse model:

$$T_o = \left[\frac{F_S(1-A)}{4\sigma\left(1 - \frac{f}{2}\right)} \right]^{\frac{1}{4}}$$

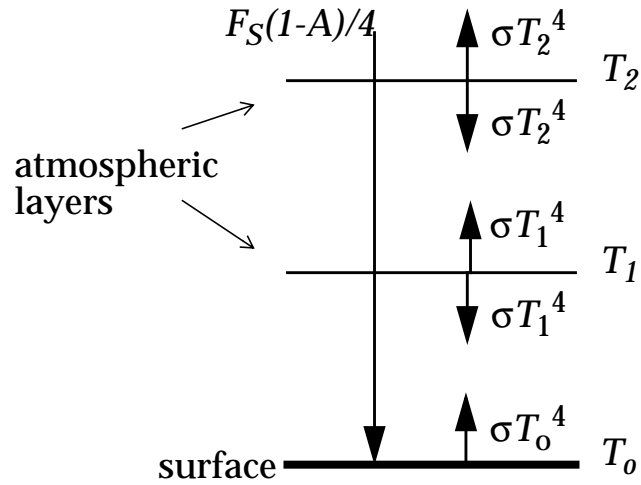
The present-day solar constant F_S is 1370 W m^{-2} ; 3.8 billion years ago it was $0.75 \times 1370 = 1030 \text{ W m}^{-2}$. Replacing in the above equation, and assuming the same albedo (A) and atmospheric composition (f) as today, we obtain:

$$T_o = \left[\frac{1030 \times (1 - 0.28)}{4 \times 5.7 \times 10^{-8} \times \left(1 - \frac{0.77}{2}\right)} \right]^{\frac{1}{4}} = 270 \text{ K}$$

which is too cold for liquid water to be present.

2. 100% absorption of terrestrial radiation is represented in our simple model by $f = 1$. Replacing in the above equation, with other numerical values the same, we obtain $T_o = 284 \text{ K}$. This is sufficient to maintain liquid water.

3. In a thick greenhouse atmosphere, radiation emitted by the atmosphere is reabsorbed by the atmosphere above it. We can represent this situation in our simple greenhouse model by considering two superimposed atmospheric layers, each absorbing 100% of terrestrial/atmospheric radiation:



The energy balance equation for the (Earth + atmosphere) system is

$$\frac{F_S(1-A)}{4} = \sigma T_2^4 \quad (1)$$

The energy balance equation for atmospheric layer 2 is

$$\sigma T_1^4 = 2\sigma T_2^4 \quad (2)$$

The energy balance equation for atmospheric layer 1 is

$$\sigma T_o^4 + \sigma T_2^4 = 2\sigma T_1^4 \quad (3)$$

From equations (2) and (3) we obtain

$$\sigma T_o^4 = 3\sigma T_2^4$$

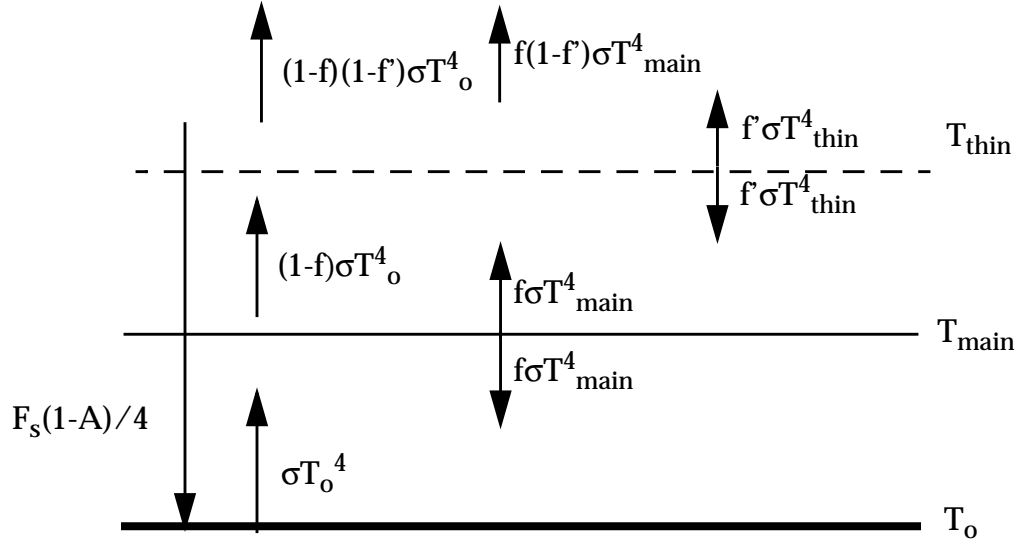
and replacing into (1):

$$T_o = \left[\frac{3F_S(1-A)}{4\sigma} \right]^{\frac{1}{4}}$$

Substituting numerical values we obtain $T_o = 314$ K (warm!). We see how a thick greenhouse atmosphere can compensate for a weaker Sun.

4. In the present Earth, atmospheric CO_2 is taken up by the oceans and by the biosphere. In an Earth covered with ice these sinks would not operate. Therefore CO_2 would accumulate in the atmosphere.

7.5 Planetary skin



For the “thin” atmospheric layer, $f' \ll 1 \Rightarrow (1 - f') \approx 1$. We use this approximation in what follows. The radiative flux balance equation for the (Earth + atmosphere) system is given by

$$F_s \frac{(1-A)}{4} = (1-f)\sigma T_o^4 + f\sigma T_{main}^4 + f'\sigma T_{thin}^4 \quad (1)$$

and the radiative flux balance equation for the thin atmospheric layer is given by

$$f'[(1-f)\sigma T_o^4 + f\sigma T_{main}^4] = 2f'\sigma T_{thin}^4 \quad (2)$$

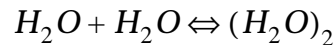
Replacing (2) into (1):

$$F_s \frac{(1-A)}{4} = 2\sigma T_{thin}^4 + f'\sigma T_{thin}^4 = \sigma T_{thin}^4(2 + f') = 2\sigma T_{thin}^4$$

Substituting numerical values ($F_s = 1370 \text{ W m}^{-2}$, $A = 0.28$, $\sigma = 5.7 \times 10^{-8} \text{ W m}^{-2} \text{ }^\circ\text{K}^{-4}$) we obtain $T_{thin} = 217 \text{ K}$. In an atmosphere that doesn't absorb solar radiation this is the coldest temperature that can be achieved, corresponding to heating from below but no heating from above. Indeed, this “skin” temperature corresponds roughly to the range of temperatures observed near the tropopause. At higher altitudes, absorption of solar radiation by the stratospheric ozone layer provides a local source of heat.

7.6 Absorption in the atmospheric window

1. The water vapor dimer is in equilibrium with water vapor,



with an equilibrium constant $K = [(H_2O)_2]/[H_2O]^2$. The absorption coefficient from the water vapor dimer is proportional to the dimer column concentration, which in turn is proportional (from the equilibrium constant) to the square of the water vapor concentration. So $k \sim p^2$.

2. The optical depth $d\delta$ from absorption by the water vapor dimer in an elemental horizontal slab of

thickness dz is given by

$$d\delta = k\rho dz$$

where k is the absorption coefficient given in units of m^2 per kg of air, and ρ is the mass density of air (kg m^{-3}). We have $k = \alpha p^2$ where $\alpha = 1 \times 10^{-11} \text{ m}^2 \text{ kg}^{-1} \text{ Pa}^{-2}$. Let C denote the mixing ratio of water vapor, $h = 4 \text{ km}$ the corresponding scale height, P the atmospheric pressure, and P_o the atmospheric pressure at sea level:

$$p = CP = C_o P_o \exp\left[-z\left(\frac{1}{h} + \frac{1}{H}\right)\right] = p_o \exp\left[-z\left(\frac{1}{h} + \frac{1}{H}\right)\right]$$

We therefore have:

$$d\delta = k\rho_a dz = \alpha\left(p_o^2 \exp\left[-2z\left(\frac{1}{h} + \frac{1}{H}\right)\right]\right)\rho_o \exp\left[-\frac{z}{H}\right] dz = \alpha\rho_o p_o^2 \exp\left[-z\left(\frac{2}{h} + \frac{3}{H}\right)\right] dz$$

We now integrate over the depth of the atmosphere to obtain the total optical depth δ :

$$\delta = \int d\delta = \int_0^{\infty} \alpha\rho_o p_o^2 \exp\left[-z\left(\frac{2}{h} + \frac{3}{H}\right)\right] dz = \frac{\alpha\rho_o p_o^2}{\left(\frac{2}{h} + \frac{3}{H}\right)} = \frac{1 \times 10^{-11} \cdot 1.2 \cdot 1 \times 10^6}{\frac{2}{4 \times 10^3} + \frac{3}{7.4 \times 10^3}} = 0.013$$

The water vapor dimer absorbs only 1.3% of the incoming radiation; it is not an efficient absorber.

SOLUTIONS TO PROBLEMS, CHAPTER 8

8. 1 Lifetime of aerosols

1. At steady state, the loss rate L of ^{210}Pb from deposition balances the ^{222}Rn emission rate, which is $1.0 \text{ atoms cm}^{-2} \text{ s}^{-1}$ over 30% of the Earth's surface area $4\pi R^2 = 5.1 \times 10^8 \text{ km}^2$:

$$L = 1.0 \times 0.3 \times 5.1 \times 10^{18} = 1.5 \times 10^{18} \text{ atoms s}^{-1}$$

The mass of ^{210}Pb in the troposphere is $380 \text{ g} = (380/210) \times 6.023 \times 10^{23} = 1.09 \times 10^{24} \text{ atoms}$

Therefore the residence time of ^{210}Pb -carrying aerosols in the troposphere is $1.09 \times 10^{24} / 1.5 \times 10^{18} = 7.3 \times 10^5 \text{ s} = 8.4 \text{ days}$.

2. We write the steady-state mass balance equations for ^7Be in the stratosphere (m_S) and in the troposphere (m_T):

$$\begin{aligned} P_S &= (k_c + k_{ST})m_S \\ P_T + k_{ST}m_S &= (k_c + k_d)m_T \end{aligned}$$

where P_S and P_T are the production rates of ^7Be in the stratosphere and troposphere, respectively; $k_c = 4.7 \text{ yr}^{-1}$ is the rate constant for radioactive decay; and k_d is the unknown rate constant for deposition in the troposphere. We have neglected the transfer of ^7Be from the troposphere to the stratosphere, which must be negligibly small in view of the short lifetimes of tropospheric ^7Be against radioactive decay and deposition. From the two equations we derive an expression for k_d .

$$\begin{aligned} k_d &= \frac{P_T + \frac{k_{ST}}{k_c + k_{ST}} P_S}{m_T} - k_c \\ &= \frac{0.3 \cdot 150 + \frac{0.8}{4.7 + 0.8} \cdot 0.7 \cdot 150}{3} - 4.7 = 15.3 \text{ yr}^{-1} \end{aligned}$$

so that the lifetime against deposition of ^7Be -carrying aerosols in the troposphere is $1/k_d = 24 \text{ days}$.

3. The large difference in lifetimes between ^{210}Pb -carrying and ^7Be -carrying aerosols in the troposphere reflects differences in the vertical distributions of the sources. The source of ^{210}Pb is mostly in the lower troposphere, while the source of ^7Be is mostly in the upper troposphere. It rains far less frequently in the upper troposphere than in the lower troposphere and therefore the lifetime of ^7Be -carrying aerosols is longer than that of ^{210}Pb -carrying aerosols. The time scale for vertical mixing in the troposphere (~1 month) is sufficiently long compared to the aerosol lifetimes that the vertical gradients in aerosol concentrations will be maintained.

4. The higher concentration of ^{210}Pb in the stratosphere results from the lack of a rainout sink in the stratosphere. It also means that the air entering the stratosphere must be relatively rich in ^{222}Rn , as would be expected if deep convection in the tropics is an important mechanism for transport from the troposphere to the stratosphere.

8. 2 Aerosols and radiation

1. An increase in sulfate aerosol concentrations would cause a decrease of T_o as less solar radiation would reach the Earth's surface (i.e., the albedo would increase).

2. The effect of the soot layer depends on its altitude. A soot layer near the surface effectively decreases the albedo of the surface (think for example of a soot layer above a snow surface) so that T_o will increase. A soot layer in the upper troposphere has a more complicated effect. On the one hand it absorbs solar radiation and reemits half of it back to space, preventing it from reaching the surface; on the other hand it absorbs terrestrial radiation and reemits half to the Earth, warming the surface.

3. Start from the radiative balance equation:

$$\frac{S(1-A)}{4} = \left(1 - \frac{f}{2}\right)\sigma T_o^4$$

Differentiate both sides, with $\varepsilon = dA$ and $\varepsilon' = df$:

$$-\frac{S\varepsilon}{4} = 4\sigma T_o^3\left(1 - \frac{f}{2}\right)dT_o - \frac{\varepsilon'}{2}\sigma T_o^4$$

Rearrange:

$$\frac{\varepsilon'}{2}\sigma T_o^4 - \frac{S\varepsilon}{4} = 4\sigma T_o^3\left(1 - \frac{f}{2}\right)dT_o$$

In order that dT_o be greater than 0, we must have

$$\frac{\varepsilon'}{2}\sigma T_o^4 > \frac{S\varepsilon}{4}$$

which by rearrangement gives

$$\frac{\varepsilon'}{\varepsilon} > \frac{S}{2\sigma T_o^4} \approx 1.8$$

SOLUTIONS TO PROBLEMS, CHAPTER 10

10.1 Shape of the ozone layer

1. Let $k(z) = q\sigma I(z)$ represent the O_2 photolysis rate constant at altitude z .

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

The actinic flux $I(z)$ is attenuated from the radiation flux I_∞ at the top of the atmosphere by the O_2 column overhead:

$$I(z) = I_\infty \exp\left[-\sigma \int_z^\infty [O_2] dz'\right]$$

We substitute for $[O_2]$ and integrate:

$$\begin{aligned} I(z) &= I_\infty \exp\left[-\sigma C_{O_2} n_a(0) \int_z^\infty e^{-z'/H} dz'\right] \\ &= F_\infty \exp[-H\sigma C_{O_2} n_a(0) e^{-z/H}] \end{aligned}$$

Replace into the equation for $R(z)$:

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

2) What is the shape of $R(z)$? We first remark that $R(z)$ is positive throughout the atmosphere and that $R(\infty) \rightarrow 0$. Is there a maximum for $R(z)$? We examine the derivative:

$$\frac{dR(z)}{dz} = q\sigma C_{O_2} n_a(0) I_\infty \left(-\frac{1}{H} + \sigma C_{O_2} n_a(0) e^{-z/H}\right) \exp\left[-\frac{z}{H} - H\sigma C_{O_2} n_a(0) e^{-z/H}\right]$$

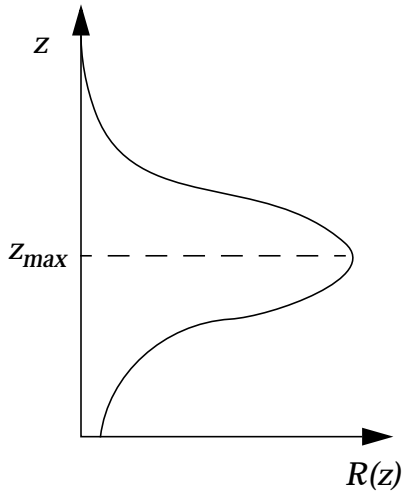
An extremum requires $dR/dz = 0$, i.e.,

$$-\frac{1}{H} + \sigma C_{O_2} n_a(0) e^{-z/H} = 0$$

which does have a positive solution:

$$z_{max} = H \ln(\sigma C_{O_2} H n_a(0))$$

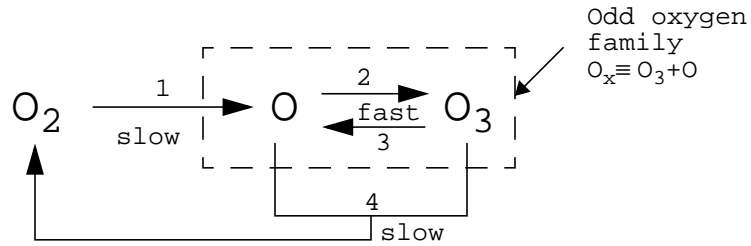
From this information we sketch $R(z)$ vs. z .



which represents qualitatively the shape of the ozone layer. $R(z)$ is the O_x production rate. The O_2 number density decreases with altitude and tends to zero towards the top of the atmosphere, while the O_2 photolysis rate constant k decreases as you penetrate down into the atmosphere and tends to zero near the surface. Therefore the product of the two must show a maximum somewhere in the atmospheric column, corresponding to the region of maximum O_x production.

10.2 Chapman mechanism

1.



Lifetime of the O atom:

$$\tau_o = \frac{[O]}{k_2[O][O_2][M]} = \frac{1}{k_2 C_{O_2} n_a^2(z)}$$

Substituting numerical values, we obtain $\tau_O = 1.5 \times 10^{-3}$ s at 20 km and $\tau_O = 2.8$ s at 45 km. The oxygen atom can be assumed to be in chemical steady state throughout the stratosphere because its chemical lifetime is so short relative to the time scales for transport.

2. $[O]/[O_3]$ is defined by the fast cycling reactions 2 & 3.



$$\frac{[O]}{[O_3]} = \frac{k_3}{k_2[O_2][M]} = \frac{k_3}{k_2 C_{O_2} n_a^2(z)}$$

@ 20 km:

$$\frac{[O]}{[O_3]} = 1.5 \times 10^{-5} \text{ mol/mol}$$

@ 45 km:

$$\frac{[O]}{[O_3]} = 0.028 \text{ mol/mol}$$

Yes, we can assume $[O_3] = [O_x]$ throughout the stratosphere.

3. O_x production = reaction 1 (x2)

O_x loss = reaction 4 (x2)

Mass balance equation for O_x :

$$\frac{d[O_x]}{dt} = 2k_1[O_2] - 2k_4[O_3][O]$$

The first term on the right hand side is the O_x production rate, and the second term contains an $[O]$ which can be substituted for using the ratio derived in part 2 of this problem:

$$\frac{d[O_x]}{dt} = P - 2k_4[O_3] \left(\frac{k_3[O_3]}{k_2 C_{O_2} n_a^2(z)} \right)$$

Also, from part 2, $[O_3] \approx [O_x]$; therefore,

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

where

$$k = \frac{2k_4 k_3}{k_2 C_{O_2} n_a^2(z)}$$

4.

$$\tau_{O_x} = \frac{[O_x]}{\text{loss}(O_x)} = \frac{[O_x]}{k[O_x]^2} = \frac{1}{k[O_x]}$$

k(20km)=

$$\frac{2(1 \times 10^{-2})(8 \times 10^{-12}) \left(\exp\left(-\frac{2060}{200}\right) \right)}{(1 \times 10^{-33})(0.21)(1.8 \times 10^{18})^2} = 7.9 \times 10^{-21} \left(\frac{\text{cm}^3}{\text{molec s}} \right)$$

$$[O_x] \cong [O_3] = 2 \times 10^{12} \left(\frac{\text{molec}}{\text{cm}^3} \right)$$

$$\tau_{O_x} = \frac{1}{(7.9 \times 10^{-21})(2 \times 10^{12})} = 2 \text{ years}$$

k(45km)=

$$\frac{2(1 \times 10^{-2})(8 \times 10^{-12}) \left(\exp\left(-\frac{2060}{270}\right) \right)}{(1 \times 10^{-33})(0.21)(4.1 \times 10^{16})^2} = 2.2 \times 10^{-16} \left(\frac{\text{cm}^3}{\text{molec s}} \right)$$

$$[O_x] \cong [O_3] = 0.2 \times 10^{12} \left(\frac{\text{molec}}{\text{cm}^3} \right)$$

$$\tau_{O_x} = 6 \text{ hours}$$

5. Chemical steady state for O_x should apply in the upper but not in the lower stratosphere. Therefore, the upper stratosphere is best for testing the Chapman mechanism by comparing observed O_3 concentrations to those predicted from chemical steady state.

10.3 The detailed Chapman mechanism

1.1 Loss of $O(^1D)$ is by reactions (5) and (6),

$$\begin{aligned} \tau_{O(^1D)} &= \frac{[O(^1D)]}{k_5[O(^1D)][N_2] + k_6[O(^1D)][O_2]} = \frac{1}{k_5[N_2] + k_6[O_2]} \\ &= \frac{1}{(k_5 C_{N_2} + k_6 C_{O_2}) n_a} = 6.6 \times 10^{-7} \text{ s} \end{aligned}$$

Steady-state for $O(^1D)$: production by reaction (3) must balance loss by reactions (5) and (6),

$$k_3[O_3] = k_5[O(^1D)][N_2] + k_6[O(^1D)][O_2] = \frac{[O(^1D)]}{\tau_{O(^1D)}}$$

so that

$$[O(^1D)] = \tau_{O(^1D)} k_3 [O_3] = 5.4 \times 10^2 \text{ molecules cm}^{-3}$$

1.2 Loss of $O(^3P)$ is by reactions (4) and (7), with rate(4) \gg rate (7):

$$\tau_{O(^3P)} = \frac{1}{k_4 [O_2] [M] + k_7 [O_3]} \approx \frac{1}{k_4 [O_2] [M]} = \frac{1}{k_4 C_{O_2} n_a^2} = 2.3 \text{ s}$$

Steady-state for $O(^3P)$: production by reactions (1), (2), (5), (6) must balance loss by reactions (4) and (7). Two simplifications can be made:

- rate(1) and rate(7) (production and loss of O_x) are small compared to the other terms (cycling of O_x)
- rate(5)+rate(6)=rate(3) (steady state for $O(^1D)$)

$$(k_2 + k_3) [O_3] = k_4 [O(^3P)] [O_2] [M]$$

so that

$$[O(^3P)] = \frac{k_2 + k_3}{k_4} \frac{[O_3]}{C_{O_2} n_a^2} = 2.4 \times 10^9 \text{ molecules cm}^{-3}$$

1.3 Calculate the lifetime of O_x . Loss of O_x is by reaction (7), which consumes two O_x molecules, and $[O_x] \approx [O_3]$:

$$\tau_{O_x} = \frac{1}{2k_7 [O(^3P)]} = 18 \text{ hours}$$

2. If O_x is in steady state (a reasonable assumption in view of the short lifetime calculated above), its total loss L_{O_x} must balance its production P_{O_x} from reaction (1):

$$L_{O_x} = P_{O_x} = 2k_1 [O_2]$$

The loss from the Chapman mechanism by reaction (7) accounts for a fraction

$$\frac{2k_7 [O(^3P)] [O_3]}{2k_1 [O_2]} = 24\% \text{ of the total } O_x \text{ loss}$$

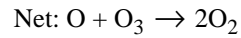
There must be therefore other sinks for O_x than the Chapman mechanism.

10.4 HO_x -catalyzed ozone loss

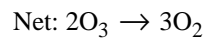
($HO_x = H, OH, HO_2$)

1. Catalytic O₃ loss cycles starting with reaction of OH:

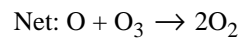
a)



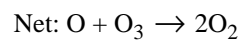
b)



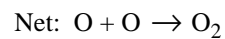
c)



d)



e)

2) The sinks for HO_x are

10.5 Chlorine chemistry at mid-latitudes

1.

$$\tau_{\text{Cl}} = \frac{[\text{Cl}]}{[\text{Cl}](k_1[\text{O}_3] + k_2[\text{CH}_4])} = \frac{1}{k_1[\text{O}_3] + k_2[\text{CH}_4]} = 3.5 \times 10^{-2} \text{ s}$$

$k_1[\text{O}_3] \gg k_2[\text{CH}_4]$, so the principal sink for Cl is reaction with O_3 .

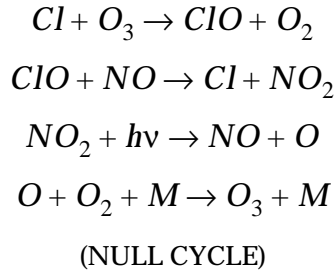
$$\tau_{\text{ClO}} = \frac{[\text{ClO}]}{[\text{ClO}](k_3[\text{O}] + k_5[\text{NO}] + k_6[\text{HO}_2] + k_7[\text{NO}_2])} =$$

$$\frac{1}{1.14 \times 10^{-3} + 3.15 \times 10^{-2} + 1.8 \times 10^{-4} + 2.86 \times 10^{-4}} = 30 \text{ s}$$

The principal sink for ClO is reaction 5, with NO.

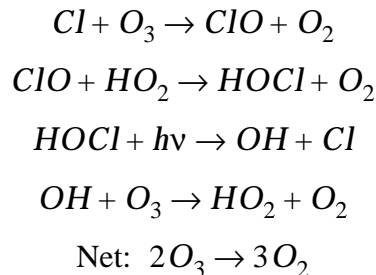
2. The Cl atoms produced from reaction (3) react mainly with O_3 to propagate the catalytic cycle. In contrast, most of the ClO molecules produced from reaction (1) react with NO instead of with O. The rate-limiting step in the catalytic cycle for O_3 loss is thus reaction (3).

3. If ClO reacts with NO, we have the reaction sequence:



This is not a catalytic cycle for O_3 loss.

4. Catalytic cycle for O_3 loss involving formation of HOCl:



The rate-limiting step for this catalytic cycle is the reaction $\text{ClO} + \text{HO}_2$ (6), while the rate-limiting step for the catalytic cycle in question 2 is $\text{ClO} + \text{O}$ (3). Each cycle results in the loss of two O_x molecules per cycle. The ratio R between the rates of O_x loss is

$$R = \frac{2k_6[\text{ClO}][\text{HO}_2]}{2k_3[\text{ClO}][\text{O}]} = \frac{k_6[\text{HO}_2]}{k_3[\text{O}]} = 0.16$$

The catalytic cycle in question 2 is six times faster.

5. Lifetime of ClO_x :

$$\tau_{\text{ClO}_x} = \frac{[\text{ClO}] + [\text{Cl}]}{k_2[\text{Cl}][\text{CH}_4] + k_6[\text{ClO}][\text{HO}_2] + k_7[\text{ClO}][\text{NO}_2]}$$

We can assume steady state for the Cl atoms,

$$\frac{[\text{Cl}]}{[\text{ClO}]} = \frac{\tau_{\text{Cl}}}{\tau_{\text{ClO}}} = 1.2 \times 10^{-3} \text{ mol/mol}$$

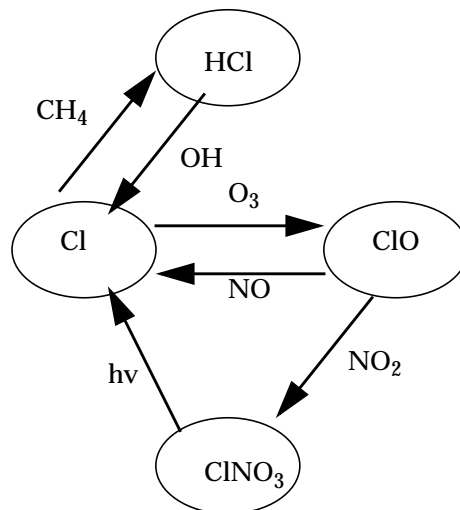
Replacing in the above expression $r = [\text{Cl}]/[\text{ClO}] = 1.2 \times 10^{-3} \text{ mol/mol}$, and noting that $r \ll 1$:

$$\begin{aligned} \tau_{\text{ClO}_x} &= \frac{1}{k_2 r [\text{CH}_4] + k_6 [\text{HO}_2] + k_7 [\text{NO}_2]} = \frac{1}{8.7 \times 10^{-6} + 1.78 \times 10^{-4} + 2.86 \times 10^{-4}} \\ &= 2.1 \times 10^3 \text{ s} = 35 \text{ min} \end{aligned}$$

This lifetime is 70 times the lifetime of ClO. We conclude that efficient cycling takes place between Cl and ClO.

10.6 Partitioning of Cl_y in the stratosphere

1.



$$\tau_{\text{Cl}} = \frac{[\text{Cl}]}{k_1[\text{Cl}][\text{O}_3] + k_5[\text{CH}_4][\text{Cl}]} = \frac{1}{k_1[\text{O}_3] + k_5[\text{CH}_4]} \approx \frac{1}{k_1[\text{O}_3]} = 0.025 \text{ s}$$

$$\tau_{ClO} = \frac{[ClO]}{k_2[ClO][NO] + k_3[ClO][NO_2]} \approx \frac{1}{k_2[NO]} = 36 \text{ s}$$

$$\tau_{ClNO_3} = \frac{1}{k_4} = 4.0 \text{ hours}$$

$$\tau_{HCl} = \frac{1}{k_6[OH]} = 12 \text{ days}$$

2. Chemical steady state for Cl atoms:

$$k_1[Cl][O_3] \approx k_2[ClO][NO] \Rightarrow \frac{[ClO]}{[Cl]} \approx \frac{k_1[O_3]}{k_2[NO]} = 1.4 \times 10^3 \text{ mol/mol}$$

Chemical steady state for ClNO₃:

$$k_3[ClO][NO_2] = k_4[ClNO_3] \Rightarrow \frac{[ClNO_3]}{[ClO]} = \frac{k_3[NO_2]}{k_4} = 28 \text{ mol/mol}$$

Therefore ClNO₃ is the main component of Cl_z. The lifetime of Cl_z is determined by the loss rate from conversion to HCl. Using the Cl_z partitioning ratios which we have just derived,

$$\begin{aligned} \tau_{Clz} &= \frac{[Cl_z]}{k_5[Cl][CH_4]} \approx \frac{1}{k_5[CH_4]} \frac{[ClNO_3]}{[Cl]} \approx \frac{1}{k_5[CH_4]} \frac{k_3[NO_2]}{k_4} \frac{k_1[O_3]}{k_2[NO]} \\ &= \frac{k_1 k_3}{k_2 k_4 k_5} \frac{[NO_2]}{[NO]} \frac{[O_3]}{[CH_4]} = 9.0 \text{ days} \end{aligned}$$

3. Since the lifetimes of the individual Cl_z species are short, equilibration within the Cl_z family is determined by the exchange between the HCl and Cl_z reservoirs. The characteristic time τ for reaching steady state in the exchange between the two reservoirs is

$$\tau = \left[\frac{1}{\tau_{HCl}} + \frac{1}{\tau_{Clz}} \right]^{-1} = 5.1 \text{ days}$$

4. Chemical steady state for HCl:

$$k_5[Cl][CH_4] = k_6[HCl][OH]$$

Also, from question 2,

$$\frac{[ClNO_3]}{[Cl]} = \frac{k_1 k_3 [NO_2]}{k_2 k_4 [NO]} [O_3]$$

We thus obtain a relationship between ClNO_3 and HCl :

$$\frac{[\text{ClNO}_3]}{[\text{HCl}]} = \frac{k_1 k_3 k_6 [\text{OH}][\text{NO}_2][\text{O}_3]}{k_2 k_4 k_5 [\text{CH}_4][\text{NO}]}$$

Consider now steady state for NO/NO_2 :

$$k_7 [\text{NO}][\text{O}_3] = k_8 [\text{NO}_2]$$

and replace into the relationship between ClNO_3 and HCl :

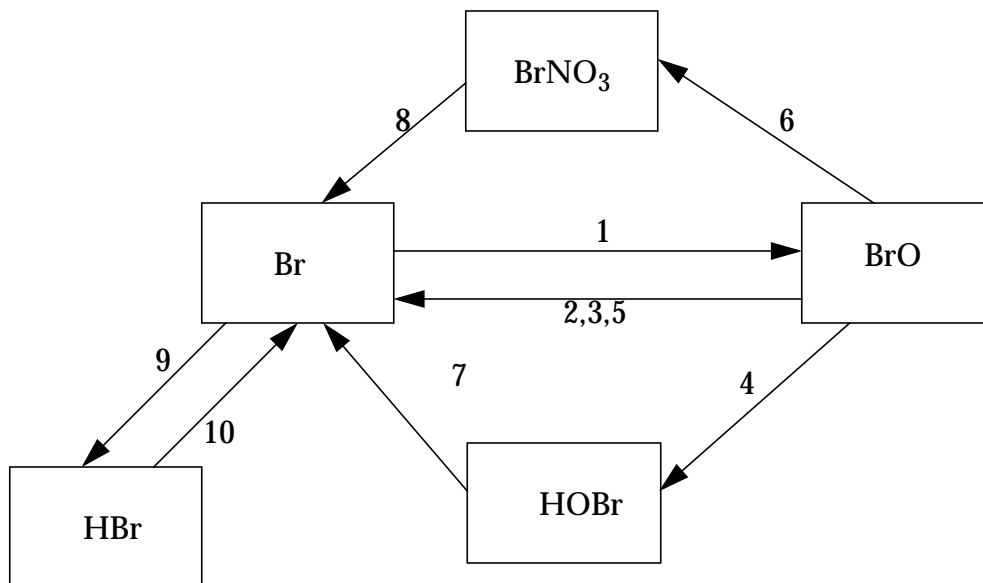
$$\frac{[\text{ClNO}_3]}{[\text{HCl}]} = \frac{k_1 k_3 k_6 k_7 [\text{OH}][\text{O}_3]^2}{k_2 k_4 k_5 k_8 [\text{CH}_4]}$$

The quadratic dependence of the ratio on $[\text{O}_3]$ reflects the compounding of two factors through which O_3 enhances ClNO_3 concentrations relative to HCl : (1) as O_3 increases, the Cl atom concentration decreases because of the $\text{Cl} + \text{O}_3$ reaction, so that formation of HCl is suppressed; (2) as O_3 increases, the NO_2 concentration increases because of the $\text{NO} + \text{O}_3$ reaction, and the resulting siphoning of ClO towards ClNO_3 further reduces the Cl atom concentration.

5. The reaction $\text{ClO} + \text{OH} \rightarrow \text{HCl} + \text{O}_2$ provides an alternate pathway for converting Cl_2 to HCl , thus decreasing the $[\text{ClNO}_3]/[\text{HCl}]$ ratio. By increasing the partitioning of Cl_y towards the inactive HCl reservoir, this reaction would slow down chlorine-catalyzed ozone loss.

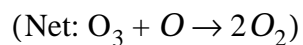
10. 7 Bromine-catalyzed ozone loss

1.

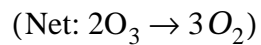
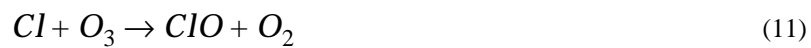


2.

(1)

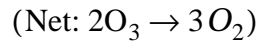


(2)



(3)





10.8 Limitation of antarctic ozone depletion

1. Steady state for Cl atoms:

$$k_2[\text{ClO}][\text{NO}] = k_1[\text{Cl}][\text{O}_3]$$

$$\frac{[\text{Cl}]}{[\text{ClO}]} = \frac{k_2[\text{NO}]}{k_1[\text{O}_3]} < \frac{k_2[\text{NO}_x]}{k_1[\text{O}_3]} = 1.7 \times 10^{-3} \text{ mol/mol}$$

Therefore $[\text{Cl}] \ll [\text{ClO}]$. Steady state for NO:

$$k_4[\text{NO}_2] = k_3[\text{NO}][\text{O}_3] + k_2[\text{ClO}][\text{NO}]$$

$$\frac{[\text{NO}]}{[\text{NO}_2]} = \frac{k_4}{k_3[\text{O}_3] + k_2[\text{ClO}]} \approx \frac{k_4}{k_3[\text{O}_3] + k_2[\text{ClO}_x]} = 2.1 \times 10^{-2} \text{ mol/mol}$$

Therefore $[\text{NO}] \ll [\text{NO}_2]$.

2. Lifetimes of Cl and NO:

$$\tau_{\text{Cl}} = \frac{[\text{Cl}]}{k_1[\text{Cl}][\text{O}_3]} = 0.06 \text{ s}$$

$$\tau_{\text{NO}} = \frac{[\text{NO}]}{k_2[\text{NO}][\text{ClO}] + k_3[\text{NO}][\text{O}_3]} = 2 \text{ s}$$

Short lifetimes -> steady state assumption is OK.

3. Loss of ClO_x is by reaction (5):

$$\tau_{\text{ClO}_x} = \frac{[\text{ClO}_x]}{k_5[\text{Cl}][\text{CH}_4]}$$

Steady state for Cl atoms:

$$[\text{Cl}] = \frac{k_2[\text{ClO}][\text{NO}]}{k_1[\text{O}_3]} \approx \frac{k_2[\text{ClO}_x][\text{NO}]}{k_1[\text{O}_3]}$$

Steady state for NO:

$$[NO] = \frac{k_4[NO_2]}{k_3[O_3] + k_2[ClO]} \approx \frac{k_4[NO_x]}{k_3[O_3] + k_2[ClO_x]} \approx \frac{k_4[NO_x]}{k_2[ClO_x]}$$

(since $k_3[O_3] \ll k_2[ClO_x]$)

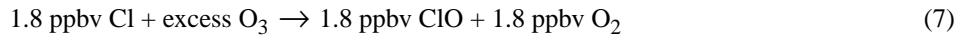
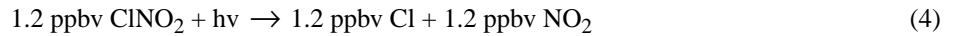
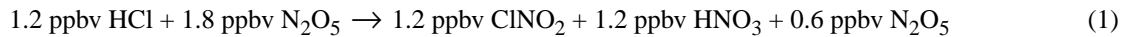
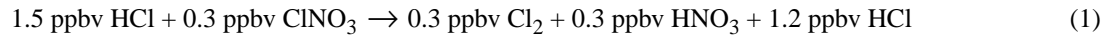
Replacing,

$$\tau_{ClO_x} = \frac{k_1[O_3][ClO_x]}{k_4 k_5 [NO_x][CH_4]}$$

Substituting numerical values, we find τ_{ClO_x} (days) = $3.8[O_3]$ (ppmv). As O_3 concentrations decrease due to ClO_x -catalyzed O_3 loss, the $[Cl]/[ClO]$ ratio increases and reaction (5) becomes increasingly effective as a ClO_x sink, limiting the extent of O_3 depletion.

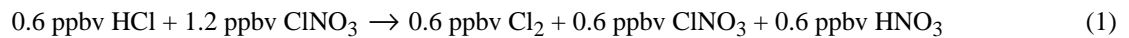
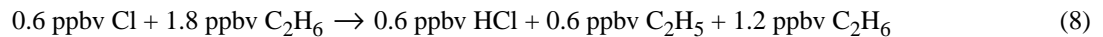
10.9 Fixing the ozone hole

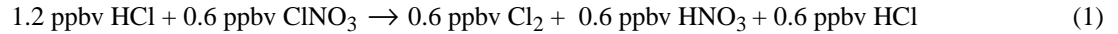
1. Input the given initial concentrations into equations (1) - (7) sequentially, canceling products and reactants as they are used up:



Thus we end up with 1.2 ppbv $ClNO_3$ and 0.6 ppbv (Cl+ClO).

2. Add 1.8 ppbv C_2H_6 after the above reactions have occurred. First, C_2H_6 reacts with the 0.6 ppbv of Cl/ClO:





Thus we end up with 1.2 ppbv(Cl+ClO), 0.6 ppbv HCl, and zero ClNO₃.

This amount of ethane injection would actually increase the amount of Cl and ClO present, thus increasing the potential for ozone loss.

3. Since we have no more ClNO₃ left to turn HCl into Cl, we can convert all Cl/ClO to HCl by adding 1.2 ppbv more C₂H₆ (total of 3 ppbv).

10. 10 PSC formation

1. Phase rule: $n = c + 2 - p$. Here $c=2$, so $p=4$ implies $n=0$. Coexistence of four phases is possible but only for specific points (not regions) in the (T, P_{H_2O}, P_{HNO_3}) space. B, D, Q are such points.

2. NAT and H₂O ice particles coexist at equilibrium along the line starting from point B. The temperature must be less than about 235 K (temperature of point B).

3.1 The PSC particles will form at about 195 K, with a composition of HNO-3H₂O (NAT).

3.2 H₂O and HNO₃ are gradually depleted from the gas phase according to the NAT stoichiometry, meaning that H₂O is being depleted three times as quickly as HNO₃. However, there is 100 times as much H₂O available, thus eventually HNO₃ will be titrated and H₂O ice will form.

SOLUTIONS TO PROBLEMS, CHAPTER 11

11. 1 Sources of CO

1. If CH_4 oxidation were the only source of CO, then the concentration of CO would be determined by the chemical steady state,

$$k_1[\text{CH}_4][\text{OH}] = k_2[\text{CO}][\text{OH}] \Rightarrow [\text{CO}] = \frac{k_1}{k_2}[\text{CH}_4] = \frac{2.5 \times 10^{-15}}{1.5 \times 10^{-13}} \cdot 1700 = 28 \text{ ppbv}$$

Therefore, CH_4 oxidation contributes $28/80 = 35\%$ of the CO source in the northern hemisphere and $28/50 = 56\%$ of the CO source in the southern hemisphere, reflecting the concentration of combustion sources in the northern hemisphere. Note that the CO lifetime is sufficiently short (2 months) that interhemispheric transport can be neglected in the CO budget for each hemisphere.

11. 2 Estimating the global source of tropospheric ozone

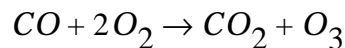
1.

The net source F_{ST} of tropospheric ozone contributed by transport from the stratosphere is given by

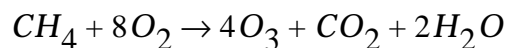
$$F_{ST} = k_{ST}N_{O_3S} - k_{TS}N_{O_3T} = (k_{ST}f_S + k_{TS}(1 - f_S))N_{O_3}$$

where $N_{O_3} = 5 \times 10^{13}$ moles is the total amount of O_3 in the atmosphere and $f_S = 0.9$ is the stratospheric fraction. Substituting numerical values we find $F_{ST} = 3 \times 10^{13}$ moles yr^{-1} .

2.1 Net reaction for oxidation of CO to CO_2 :



Net reaction for oxidation of CH_4 to CO_2 :



So, the yields are 4 molecules of ozone per molecule of methane oxidized and 1 molecule of ozone per molecule of carbon monoxide oxidized.

2.2

$$4(3 \times 10^{13}) + 1(4 \times 10^{13}) = 1.6 \times 10^{14} \text{ moles yr}^{-1}$$

2.3 Our simple model assumed high- NO_x conditions and hence an upper limit for the O_3 yield from oxidation of CO and CH_4 . In the more complicated models of the actual atmosphere, reactions of peroxy radicals with species other than NO (such as for example the $\text{HO}_2 + \text{HO}_2$ reaction) will reduce the O_3 yield.

2.4 Chemical production within the troposphere is the dominant source of tropospheric ozone.

11. 3 Oxidizing power of the atmosphere

1.1 Calculate how many CH_3O_2 molecules are produced by oxidizing one methane molecule to CO_2 .

a. 1 molecule CH_3O_2 is produced in (1)

b. $2/3$ of this CH_3O_2 reacts by (2a), producing $2/3$ molecule CH_3OOH

c. this $2/3$ molecule CH_3OOH reacts by (3); $1/3$ of it, or $(2/3)(1/3) = 2/9$, reacts by (3c), producing $2/9$ molecule CH_3O_2

d. $2/3$ of this CH_3O_2 reacts by (2a), i.e., step b., and the cycle continues indefinitely, each time producing $(2/9)^n \text{CH}_3\text{O}_2$, where $n=\{0,1,2,\dots\}$

We thus have an infinite series $1 + x + x^2 + x^3 + \dots = 1/(1-x)$ with $x=2/9$. The total CH_3O_2 produced is $9/7 = 1.29$

1.2 OH is consumed in reactions 1, 3c, 4c, and 5; it is produced in reaction 3a (3b has no net effect).

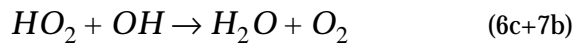
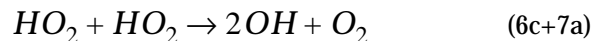
Net OH consumed = (1) + (5) + (2a)(3c) + (4c) - (2a)(3a) = $1 + 1 + (9/7)(2/3)(1/3) + 1/4 - (9/7)(2/3)(1/3) = 2.25$ molecules consumed.

1.3 Net HO_2 produced? HO_2 consumed in reaction 2a but produced in reactions 2b, 3a, 4a (2x), 4c, and 5.

Net produced = $-(2a) + (2b) + (2a)(3a) + 2(4a) + (4c) + (5) = -(9/7)(2/3) + (9/7)(1/3) + (9/7)(2/3)(1/3) + 2(1/2) + 1/4 + 1 = 2.11$

1.4 $2.25 - 2.11 = 0.14$ molecules of HO_x are consumed in oxidizing one molecule CH_4 to CO_2 . If more NO_x were present to favor (2b) over (2a), the oxidation of CH_4 would become a net HO_x source.

2.1 The net effect of H_2O_2 formation on the recycling of HO_2 to OH can be determined by adding (6c) and the two reaction branches for H_2O_2 :



What fraction of HO_2 is recycled to OH? = (6a) + (6b) + (6c)(7a) - (6c)(7b) = $1/4 + 1/4 + (1/2)(1/2) - (1/2)(1/2) = 0.5$ or 50%

2.2 From methane to CO_2 , 50% of the 2.11 HO_2 is actually recycled to OH, so that only 1.06 OH are actually consumed. From CO to CO_2 , 0.5 OH consumed.

2.3 Current OH source from photolysis = 2.9×10^{11} molecules $\text{cm}^{-2} \text{s}^{-1}$. Current OH consumption from oxidation of CH_4 and CO = $1.06(1.2 \times 10^{11}) + 0.5(1.9 \times 10^{11}) = 2.2 \times 10^{11}$ molecules $\text{cm}^{-2} \text{s}^{-1}$. There is enough OH supplied to oxidize CH_4 and CO.

What if methane emissions doubled? the additional OH consumption rate of $1.06(1.2 \times 10^{11})$ molecules $\text{cm}^{-2} \text{s}^{-1}$ would bring the total OH consumption rate to 3.5×10^{11} molecules $\text{cm}^{-2} \text{s}^{-1}$; OH would be titrated.

If CO emissions doubled, the additional OH consumption rate of $0.5(1.9 \times 10^{11})$ molecules $\text{cm}^{-2} \text{s}^{-1}$ would

bring the total OH consumption rate to 3.2×10^{11} molecules $\text{cm}^{-2} \text{s}^{-1}$; OH would be titrated.

2.4 If OH and HO_2 were to decrease, the branching ratios would change. 2b would increase relative to 2a; 3a would increase relative to 3c; 4a would increase relative to 4c; and 7a would increase relative to 7b. All three of these effects would act as negative feedbacks to prevent total titration of OH. For the branching ratios given in this problem, the effect on the branching ratio of (2) would be most important in view of the present dominance of 2a.

11. 4 OH concentrations in the past

1. Oxidation of CH_4 produces CH_2O with a yield of unity (though the route through which CH_2O is produced might vary, depending in particular on the abundance of NO_x). The lifetime of CH_2O is sufficiently short (1 day) that chemical steady state can be assumed:

$$\frac{d[\text{CH}_2\text{O}]}{dt} = k'[\text{CH}_4][\text{OH}] - k[\text{CH}_2\text{O}] = 0$$

$$\text{CH}_2\text{O} = \frac{k'}{k}[\text{CH}_4][\text{OH}]$$

2.1 Rearrange this equation to solve for [OH]:

$$[\text{OH}] = \frac{[\text{CH}_2\text{O}]k}{[\text{CH}_4]k'}$$

Present $[\text{OH}] = 1.9 \times 10^5$ molecules cm^{-3}

Pre-industrial $[\text{OH}] = 2.3 \times 10^5$ molecules cm^{-3}

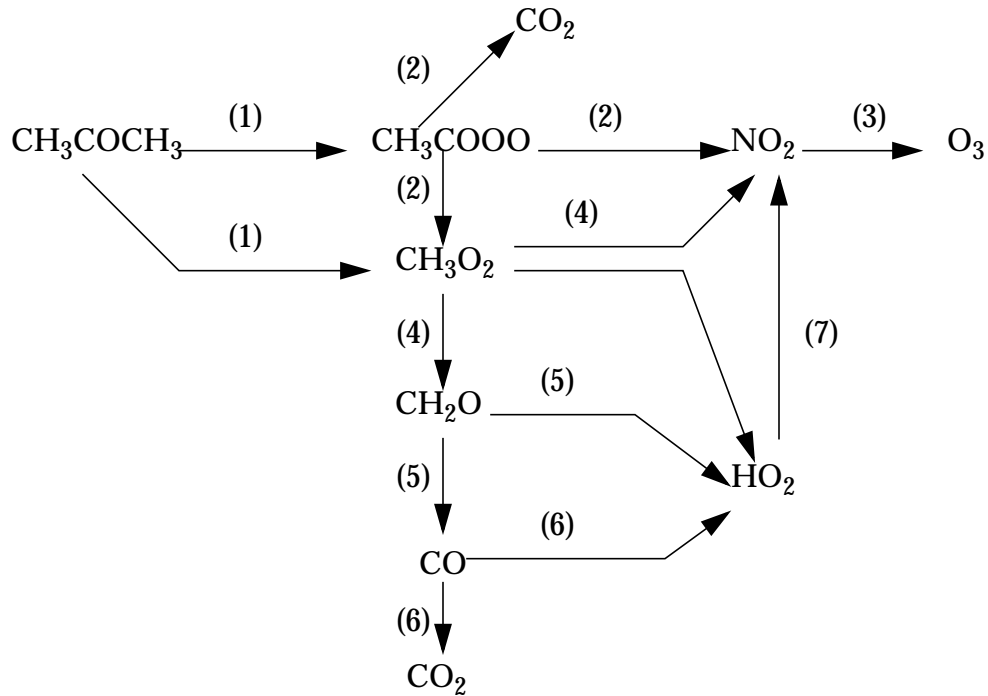
Glacial $[\text{OH}] = 1.1 \times 10^5$ molecules cm^{-3}

2.2 The OH decrease from preindustrial to today suggested by the ice core data could be explained by increases in CH_4 and CO.

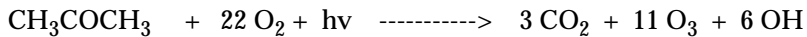
2.3 Atmospheric concentrations of N_2O , CH_4 , and H_2O were all lower in glacial times; N_2O and CH_4 because of the less active biosphere, H_2O because of the lower atmospheric temperatures. As a result, catalytic O_3 loss in the stratosphere would be less. In addition, less convective activity in the glacial period would result in a lower tropopause and a thicker stratosphere. A thicker stratospheric O_2 layer would decrease the UV flux reaching the the troposphere and therefore the production of OH in the troposphere.

11. 5 Acetone in the upper troposphere

1. How many molecules of O_3 and HOx are produced in the complete oxidation of acetone to CO_2 ?



The numbers refer to the reactions. Notice that 2 molecules of CH₃O₂ are formed, so reactions (4), (5) and (6) all proceed twice. Two CO₂ are formed from reactions (4) through (6) and one is formed from reaction (2). Two HO_x are formed when reaction (4) proceeds twice and 4 HO_x are formed when reaction (5) proceeds twice. Notice that reaction (6) contributes no net HO_x production or loss, but does convert OH to HO₂ which participates in ozone production. The number of NO₂ formed corresponds to the number of O₃ formed - 1 NO₂ is formed in reaction (2), 2 NO₂ are formed from reaction (4) taking place twice, 8 NO₂ are formed from reaction (7) with HO₂. The net reaction for this mechanism is:



2. Compare sources of HO_x from photolysis of acetone and from photolysis of O₃.

The loss rate of acetone is $k_1[\text{Acetone}]$. The corresponding HO_x source is $S_{\text{HO}_x} = nk_1[\text{Acetone}]$ where $n = 6$ is the HO_x yield from the oxidation of acetone to CO₂. Substituting numerical values we find $S_{\text{HO}_x} = 6 \times 3.7 \times 10^{-7} \times 5 \times 10^{-10} \times 8 \times 10^{18} = 9 \times 10^3$ molecules HO_x produced per acetone molecule consumed.

The HO_x source from photolysis of O₃ is $S_{\text{HO}_x} = 2k_{10}[\text{O}({}^1\text{D})][\text{H}_2\text{O}]$. From the chemical steady state equation for O(¹D),

$$[\text{O}({}^1\text{D})] = \frac{k_8[\text{O}_3]}{k_9[\text{M}] + k_{10}[\text{H}_2\text{O}]}$$

and therefore

$$S_{HO_x} = \frac{2k_{10}[H_2O]k_8[O_3]}{k_9[M] + k_{10}[H_2O]} = 3.3 \times 10^3 \text{ molecules cm}^{-3}$$

Acetone therefore dominates as a source of HO_x .

3. The reaction $O(1D)+H_2O$ is much faster in the lower troposphere (more H_2O) and in the stratosphere (more O_3) and will thus dominate there as a source of HO_x over the photolysis of acetone.

4.1. In the oxidation of one molecule of CO to CO_2 , 1 molecule of O_3 is produced and no HO_x is produced.

4.2. First, look at the ozone production rate from oxidation of CO:

$$P_{O_3} = \frac{[CO]}{\tau_{CO}} = \left(\frac{1}{3 \text{ mon}}\right) \left(\frac{1 \text{ mon}}{30 \text{ day}}\right) \left(\frac{1 \text{ day}}{86400 \text{ s}}\right) \left(\frac{100 \text{ ppb} \cdot M}{10^9}\right) = 1.1 \times 10^5 \frac{\text{molec}}{\text{cm}^3 \text{ s}}$$

Next, look at the ozone production rate from oxidation of acetone:

$$P_{O_3} = 11k_1[CH_3COCH_3] = 1.6 \times 10^4 \frac{\text{molec}}{\text{cm}^3 \text{ s}}$$

The direct source of O_3 from oxidation of acetone is minor compared to that from oxidation of CO. However, the oxidation of acetone is a major source of HO_x . Increasing acetone in the upper troposphere would increase $HO_x \rightarrow$ decrease $\tau_{CO} \rightarrow$ increase O_3 production. Ozone production in the upper troposphere is thus sensitive to acetone because of its effect on the CO oxidation rate.

11. 6 Transport, rainout, and chemistry in the marine upper troposphere

1. The residence time of air in the upper troposphere is $\tau_3 = 1/k_{32}$. The masses of air m_i in each layer are proportional to their pressure thicknesses $\Delta P_i = P_i(\text{bottom}) - P_i(\text{top})$. We therefore use ΔP_i as measure of the mass (or number of moles) of air in a layer. We obtain a relationship between k_{13} and k_{32} by considering the mass balance of air in the upper troposphere:

$$k_{13}\Delta P_1 = k_{32}\Delta P_3 \Rightarrow k_{13} = \frac{\Delta P_3}{\Delta P_1} k_{32}$$

We now apply the steady-state equation for CH_3I in the upper troposphere:

$$k_{13}[CH_3I]_1 \Delta P_1 = (k + k_{32})[CH_3I]_3 \Delta P_3$$

where the bracketed concentrations are mixing ratios as given in the problem, and $k = 0.25 \text{ day}^{-1}$ is the CH_3I photolysis rate constant. Substituting k_{13} from the first equation, we cancel the ΔP terms:

$$k_{32}[CH_3I]_1 = (k + k_{32})[CH_3I]_3$$

and obtain an expression for k_{32} :

$$k_{32} = \frac{k[CH_3I]_3}{[CH_3I]_1 - [CH_3I]_3} = \frac{0.25 \cdot 0.10}{0.36 - 0.10} = 9.6 \times 10^{-2} \text{ s}^{-1}$$

The residence time of air in the upper troposphere is therefore $\tau_3 = 1/0.096 = 10$ days.

2. By definition of the Henry's Law constant,

$$K_X = \frac{\{X\}_{aq}}{P_X}$$

where P_X is the partial pressure of X in the gas phase, and $\{X\}_{aq}$ is the cloudwater concentration in moles per unit volume of water. We use the cloud liquid water content to relate $\{X\}_{aq}$ to $[X]_{aq}$:

$$[X]_{aq} = L\{X\}_{aq}$$

and we use the Ideal Gas Law to relate P_X to $[X]_g$:

$$P_X = [X]_g RT$$

We thus obtain the relationship:

$$f = \frac{[X]_{aq}}{[X]_g} = K_X L R T$$

3. The Henry's Law constants are given in customary units of $M \text{ atm}^{-1}$. To avoid confusion, let us convert to SI units: $1 M \text{ atm}^{-1} = 1 \text{ mole l}^{-1} \text{ atm}^{-1} = 10^{-2} \text{ mole m}^{-3} \text{ Pa}^{-1}$. Substituting numerical values of K_X for H_2O_2 and CH_3OOH , we obtain $f_{\text{H}_2\text{O}_2} = 2 \times 10^3 \times 1 \times 10^{-6} \times 8.31 \times 250 = 4.2$ and $f_{\text{CH}_3\text{OOH}} = 0.06$. We find that H_2O_2 in a cloud fractionates preferentially in the cloudwater and is therefore efficiently scavenged by rainout; in contrast, CH_3OOH is not efficiently scavenged.

4. The net source $S_{\text{CH}_3\text{OOH}}$ (molecules $\text{cm}^{-3} \text{ s}^{-1}$) of CH_3OOH to the upper troposphere by deep convection is

$$\begin{aligned} S_{\text{CH}_3\text{OOH}} &= n_a k_{32} ([\text{CH}_3\text{OOH}]_1 - [\text{CH}_3\text{OOH}]_3) = 4 \times 10^{18} \cdot \frac{0.1}{86400} \cdot (1100 - 80) \cdot 10^{-12} \\ &= 5 \times 10^3 \text{ molecules cm}^{-3} \text{ s}^{-1} \end{aligned}$$

5. Yield of $\text{HO}_x = 2x(1a) + 2x(2b) = 2(1/2) + 2(1/3) = 1.7$

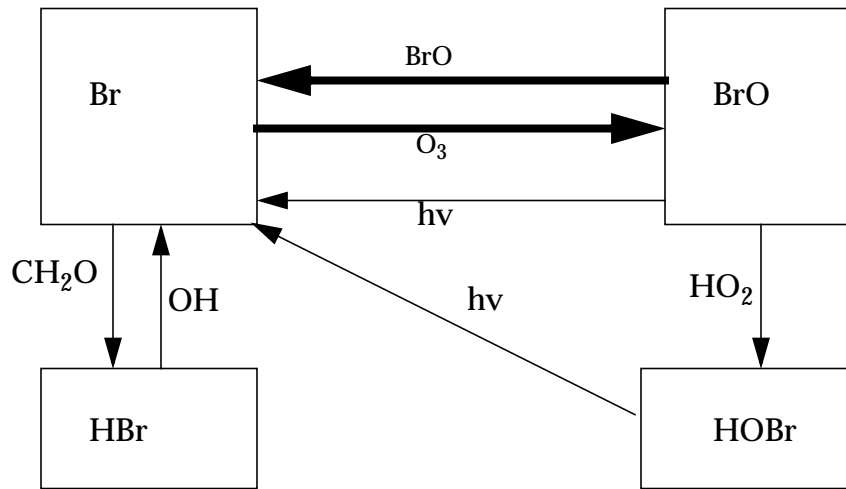
The resulting source of HO_x is

$$S_{\text{HO}_x} = (\text{HO}_x \text{ yield}) S_{\text{CH}_3\text{OOH}} = 1.7 \times 5 \times 10^3 = 8.5 \times 10^3 \text{ molecules cm}^{-3} \text{ s}^{-1}.$$

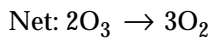
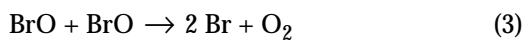
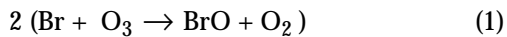
This source is comparable to the HO_x source of 1×10^4 molecules $\text{cm}^{-3} \text{ s}^{-1}$ from the $\text{O}(^1\text{D}) + \text{H}_2\text{O}$ reaction. Convective injection of CH_3OOH is therefore an important source of HO_x in the upper troposphere.

11. 7 Catalytic ozone destruction in the troposphere

1.



Catalytic O_3 loss mechanism:



2. Reactions 2, 3, and 5 are sinks for BrO:

$$\frac{\text{rate}2}{\text{rate}3} = \frac{k_2}{2k_3[\text{BrO}]} > \frac{k_2}{2k_3[\text{Br}_y]} = \frac{1 \times 10^{-2}}{2 \cdot 3 \times 10^{-12} \cdot 50 \times 10^{-12} \cdot 3 \times 10^{19}} = 1.1$$

$$\frac{\text{rate}2}{\text{rate}5} = \frac{k_2}{k_5[\text{HO}_2]} = 67$$

So reaction (2) is the principal BrO sink. Now, consider the Br sinks:

$$\frac{\text{rate}1}{\text{rate}4} = \frac{k_1[\text{O}_3]}{k_4[\text{CH}_2\text{O}]} = 4$$

Most of the cycling between Br and BrO therefore takes place by (1)+(2), which is a null cycle. Since the rate of catalytic O_3 loss by (1)+(3) is determined by the competition between (2) and (3) for BrO, reaction (3) is the limiting step for catalytic O_3 loss.

3. Since reaction (3) is the rate-limiting step for O_3 loss:

$$\frac{-d[\text{O}_3]}{dt} = 2k_3[\text{BrO}]^2$$

Assuming that $[\text{BrO}] \approx [\text{Br}_y] = 50$ pptv, we find

$-d[O_3]/dt = 2 \times 3 \times 10^{-12} \times (50 \times 10^{-12} \times 3 \times 10^{19})^2 = 1.4 \times 10^7 \text{ molecules cm}^{-3} \text{ s}^{-1} = 39 \text{ ppbv day}^{-1}$. There would be near-total O_3 depletion on a time scale of a day.

4.1 HBr and HOBr are non-radical reservoirs for Br_y ; formation of HBr and HOBr will decrease the fraction of Br_y present as BrO and therefore decrease the O_3 loss rate.

4.2 We saw in question 2 that Br and BrO are mostly cycled between each other by reactions (1) and (2). The steady-state equation for Br atoms is therefore approximately

$$k_1[Br][O_3] \approx k_2[BrO] \Rightarrow \frac{[Br]}{[BrO]} \approx \frac{k_2}{k_1[O_3]} = 0.014 \text{ mol/mol}$$

This is one relationship between Br_y species. We can get a second one from the steady-state equation for HOBr:

$$k_5[BrO][HO_2] = k_7[HOBr] \Rightarrow \frac{[HOBr]}{[BrO]} = \frac{k_5[HO_2]}{k_7} = 1.5 \text{ mol/mol}$$

and a third one from the steady-state equation for HBr:

$$\begin{aligned} k_4[Br][CH_2O] = k_6[HBr][OH] &\Rightarrow \frac{[HBr]}{[Br]} = \frac{k_4[CH_2O]}{k_6[OH]} = 160 \text{ mol/mol} \\ &\Rightarrow \frac{[HBr]}{[BrO]} = 160 \cdot 0.014 = 2.2 \text{ mol/mol} \end{aligned}$$

Finally we have the mass conservation equation for $[Br_y]$:

$$\begin{aligned} [Br_y] &= [Br] + [BrO] + [HOBr] + [HBr] \\ &\Rightarrow \frac{[Br_y]}{[BrO]} = \frac{[Br]}{[BrO]} + 1 + \frac{[HOBr]}{[BrO]} + \frac{[HBr]}{[BrO]} = 4.7 \text{ mol/mol} \end{aligned}$$

The 50 pptv Br_y are therefore partitioned into 11 pptv BrO, 16 pptv HOBr, 23 pptv HBr, and 0.15 pptv Br. The O_3 loss rate is $4.7^2 = 22$ times slower than calculated in question 3. Ozone loss is now only $1.8 \text{ ppbv day}^{-1}$ and there would be little O_3 depletion on a time scale of a few days.

4.3 The aerosol reaction $HBr + HOBr$, followed by Br_2 photolysis, converts Br_y from its non-radical inactive reservoirs into the Br/BrO radicals active in catalyzing O_3 loss. This mechanism is analogous to the aerosol reaction $HCl + ClNO_3$ taking place in the polar stratosphere.

11. 8 Nighttime oxidation of NO_x

1. The mechanism operates only at night because NO_3 would photolyze back to NO_x in the daytime.
2. Conversion of NO_2 to NO takes place only by photolysis, which does not operate at night; however, conversion of NO to NO_2 by reaction (1) still takes place at night. Therefore, NO_x at night is present entirely as NO_2 .
3. Calculate the lifetime of NO_3^* at night:

$$\tau_{NO_3^*} = \frac{[NO_3] + [N_2O_5]}{k_4[N_2O_5]} = \frac{1}{k_4} \left(1 + \frac{[NO_3]}{[N_2O_5]} \right)$$

Equilibrium (3) gives

$$\frac{[NO_3]}{[N_2O_5]} = \frac{1}{K_3[NO_2]}$$

$$\text{so } \tau_{NO_3^*} = \frac{1}{k_4} \left(1 + \frac{1}{K_3[NO_2]} \right) = 2.0 \text{ hours}$$

Here we have used the data on pressure and temperature to calculate $n_a = 2.3 \times 10^{19}$ molecules cm^{-3} and convert the mixing ratios to number densities.

4. Since NO_3^* is in steady state, reaction (2) is the effective sink for NO_x , and represents the loss of two NO_x molecules (because NO_3 combines with NO_2 to consume an additional NO_x molecule). Therefore the lifetime of NO_x at night is

$$\tau_{NO_x} = \frac{[NO_x]}{2k_2[NO_2][O_3]} = \frac{1}{2k_2[O_3]} = 7.5 \text{ hours}$$

The mechanism takes place only at night; therefore, for a 12-hour night, the lifetime of NO_x averaged over 24 hours is $7.5 \times (24/12) = 15$ hours. This lifetime is comparable to the 1-day lifetime of NO_x against oxidation by OH. Both sinks are of comparable importance.

11.9 Peroxyacetylnitrate (PAN) as a reservoir for NO_x

1. Steady state for NO:

$$k_1 [NO][O_3] = k_2 [NO_2]$$

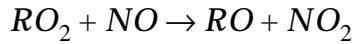
$$\frac{[NO_2]}{[NO]} = \frac{k_1 [O_3]}{k_2}$$

Replace into $[NO_x] = [NO] + [NO_2]$:

$$\frac{[NO_2]}{[NO_x]} = \frac{1}{\left(1 + \frac{k_2}{k_1 [O_3]} \right)}$$

The air density is $n_a = \frac{P}{RT} = \frac{6.023 \times 10^{23} \times 1 \times 10^5}{(8.32 \times 298)} = 2.4 \times 10^{25}$ molecules $\text{m}^{-3} = 2.4 \times 10^{19}$ molecules cm^{-3} . So $[O_3] = 100 \text{ ppbv} = 2.4 \times 10^{12}$ molecules cm^{-3} . Replacing numerical values for k_1 and k_2 (noon), we obtain $[NO_2]/[NO_x] = 0.81$. Further replacing $[NO_x] = 100 \text{ ppbv}$ we obtain $[NO_2] = 81 \text{ ppbv}$ and $[NO] = 19 \text{ ppbv}$.

At other times of the day k_2 will be smaller, so $[\text{NO}_2]/[\text{NO}_x]$ will increase. The presence of peroxy radicals will also increase the $[\text{NO}_2]/[\text{NO}_x]$ ratio by providing an additional pathway for conversion of NO to NO_2 :



2. Steady state for PAN:

$$k_{4b}[\text{CH}_3\text{C}(\text{O})\text{OO}][\text{NO}_2][\text{M}] = k_5[\text{PAN}]$$

Steady state for the $[\text{PAN} + \text{CH}_3\text{C}(\text{O})\text{OO}]$ family:

$$k_3[\text{CH}_3\text{C}(\text{O})\text{CH}_3] = k_{4a}[\text{CH}_3\text{C}(\text{O})\text{OO}][\text{NO}]$$

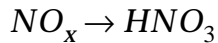
Replace, and use $[\text{NO}_2]/[\text{NO}]$ from question 1:

$$[\text{PAN}] = \frac{k_3 k_{4b}}{k_{4a} k_5} [\text{CH}_3\text{C}(\text{O})\text{CH}_3] \frac{[\text{NO}_2]}{[\text{NO}]} = \frac{k_1 k_3 k_{4b}}{k_2 k_{4a} k_5} [\text{CH}_3\text{C}(\text{O})\text{CH}_3][\text{O}_3]$$

We see that the PAN concentration increases with increasing acetone and O_3 but is insensitive to NO_x .

To explain this result qualitatively, we note that NO_x both suppresses PAN formation by reaction (4a) and promotes PAN formation by reaction (4b). Thus PAN formation depends not on the total NO_x concentration, but on the $[\text{NO}_2]/[\text{NO}]$ ratio which determines the branching ratio (4b:4a). We saw in question 1 that the $[\text{NO}_2]/[\text{NO}]$ ratio is proportional to the O_3 concentration, and hence PAN increases with increasing O_3 .

3. We introduce the schematic reaction (6),



with $d[\text{HNO}_3]/dt = -d[\text{NO}_x]/dt = k_6[\text{NO}_x]$, and $k_6 = 1 \text{ d}^{-1}$.

3.1 The mass balance equation for NO_x is

$$-\frac{d[\text{NO}_x]}{dt} = -k_6[\text{NO}_x]$$

Integration yields:

$$[\text{NO}_x] = [\text{NO}_x]_0 e^{-k_6 t}$$

with the initial condition $[\text{NO}_x]_0 = 100 \text{ ppbv}$ at time $t = 0$. After 10 days, $[\text{NO}_x] = 100 e^{-10} = 4.5 \times 10^{-3} \text{ ppbv} = 4.5 \text{ pptv}$ (small!).

3.2.1. Accounting for PAN formation, the lifetime of NO_x is given by:

$$\tau_{\text{NO}_x} = \frac{1}{k_6 + k_{4b}[\text{CH}_3\text{C}(\text{O})\text{OO}]} \frac{[\text{NO}_2]}{[\text{NO}_x]} \approx \frac{1}{k_6 + k_{4b}[\text{CH}_3\text{C}(\text{O})\text{OO}]}$$

where we have made use of the approximation $[\text{NO}] \ll \{\text{NO}_2\} \Rightarrow [\text{NO}_2]/[\text{NO}_x] \approx 1$. Replacing numerical values we obtain $\tau_{\text{NO}_x} = 35$ minutes; loss of NO_x is dominated by conversion to PAN.

The lifetime of PAN is $\tau_{\text{PAN}} = 1/k_5$. At 298 K, $k_5 = 3.6 \times 10^{-4} \text{ s}^{-1}$ and $\tau_{\text{PAN}} = 47$ minutes; at 260 K, $k_5 = 4.6 \times 10^{-7} \text{ s}^{-1}$ and $\tau_{\text{PAN}} = 25$ days.

3.2.2. Formation of PAN leads to a chemical source of NO_x in the air parcel by the reverse reaction (5). Considering that the lifetime of NO_x ($\tau_{\text{NO}_x} = 35$ minutes) is short relative to the 10-day integration time, we can assume quasi steady state for NO_x :

$$k_{4b}[\text{CH}_3\text{C}(\text{O})\text{OO}][\text{NO}_x] + k_6[\text{NO}_x] = k_5[\text{PAN}]$$

so that

$$[\text{PAN}] = \frac{k_{4b}[\text{CH}_3\text{C}(\text{O})\text{OO}][\text{NO}_x]}{k_5}$$

where we have made the approximations $[\text{NO}_2]/[\text{NO}_x] \approx 1$ and $k_{4b}[\text{CH}_3\text{C}(\text{O})\text{OO}] \gg k_6$. Let us define the chemical family $\text{NO}_x^* = \text{NO}_x + \text{PAN}$; from the above equation, we derive

$$[\text{NO}_x] = \frac{[\text{NO}_x^*]}{1 + \frac{k_{4b}[\text{CH}_3\text{C}(\text{O})\text{OO}]}{k_5}}$$

Replacing numerical values, we find that the initial 100 ppbv NO_x^* in the air parcel at time $t = 0$ quickly partition into 43 ppbv NO_x and 57 ppbv PAN; further temporal evolution of NO_x and PAN over the 10-day period is governed by slow conversion of NO_x to HNO_3 . Consider the mass balance equation for NO_x^* , for which the only loss is reaction (6):

$$\frac{d[\text{NO}_x^*]}{dt} = -k_6[\text{NO}_x]$$

Replace in this equation the above quasi steady-state equation for $[\text{NO}_x]$:

$$\left(1 + \frac{k_{4b}[\text{CH}_3\text{C}(\text{O})\text{OO}]}{k_5}\right) \frac{d[\text{NO}_x^*]}{dt} = -k_6[\text{NO}_x^*]$$

so that

$$\frac{d[NO_x]}{dt} = -\frac{k_6}{1 + \frac{k_{4b}CH_3COOO}{k_5}}[NO_x]$$

Thus the temporal evolution of the NO_x concentration is given by:

$$[NO_x] = [NO_x]_0 e^{-\frac{t}{\tau_{NO_x}^*}}$$

where $[NO_x]_0 = 43$ ppbv (the initial concentration following equilibration with PAN) and where

$$\tau_{NO_x}^* = \frac{1 + \frac{k_{4b}CH_3COOO}{k_5}}{k_6}$$

is an effective lifetime for NO_x . Inserting numerical values we obtain $\tau_{NO_x}^* = 2.3$ days. Compared to the atmosphere without PAN formation, where the lifetime of NO_x was $\tau_{NO_x} = 1/k_6 = 1$ day, the formation of PAN initially decreased the NO_x concentration from 100 ppbv to 43 ppbv but then subsequently increased the effective lifetime of NO_x by a factor 2.3. After 10 days, $[NO_x] = 43e^{-10/2.3} = 0.56$ ppbv. This is two orders of magnitude higher than the value calculated in question 3.1, ignoring PAN formation!

3.2.3. The same equations apply to 260 K (we can still assume quasi steady state for NO_x) but now k_5 is much lower. Replacing numerical values we find that the initial partitioning of NO_x^* between NO_x and PAN yields 0.10 ppbv NO_x and 99.9 ppbv PAN. The effective lifetime of NO_x is $\tau_{NO_x}^* = 2.8$ years! Thus NO_x remains constant at 0.10 ppbv over the 10-day period, less than in the previous calculation but still much more than in the calculation without PAN formation. When the temperature eventually rises, PAN will decompose and NO_x will increase.

3.2.4 We saw in this problem the importance of PAN formation in facilitating the long-range transport of NO_x in the atmosphere, both at warm and cold temperatures. At warm temperatures, formation of PAN increases the effective lifetime of NO_x . At cold temperatures, formation of PAN maintains a background NO_x concentration and provides a reservoir to eventually deliver NO_x to the atmosphere when the temperature rises.

11. 10 Photochemical equilibrium of NO_x and HNO_3

1. The lifetime of NO_x is

$$\tau_{NO_x} = \frac{[NO_x]}{k_3[NO_2][OH]} = \frac{\frac{[NO]}{[NO_2]} + 1}{k_3[OH]}$$

Assuming chemical steady state for NO, and using the approximation rate(2) >> rate(3):

$$k_1[NO][O_3] = k_2[NO_2]$$

Replacing in the expression for the NO_x lifetime:

$$\tau_{\text{NO}_x} = \frac{\frac{[\text{NO}]}{[\text{NO}_2]} + 1}{k_3[\text{OH}]} = \frac{\frac{k_2}{k_1[\text{O}_3]} + 1}{k_3[\text{OH}]}$$

The lifetime of HNO_3 is given by

$$\tau_{\text{HNO}_3} = \frac{1}{k_4[\text{OH}] + k_5}$$

At 2 km ($T = 287$ K), $\tau_{\text{NO}_x} = 1.3$ days and $\tau_{\text{HNO}_3} = 23$ days

At 10 km ($T = 235$ K), $\tau_{\text{NO}_x} = 6.6$ days and $\tau_{\text{HNO}_3} = 19$ days

The opposite dependences of τ_{NO_x} and τ_{HNO_3} on altitude reflect the opposite Arrhenius temperature dependences of reaction (1) and reaction (4)

2. Steady state for NO_x is defined by a balance between the production rate $[\text{HNO}_3]/\tau_{\text{HNO}_3}$ and the loss rate $[\text{NO}_x]/\tau_{\text{NO}_x}$. Therefore

$$\frac{[\text{HNO}_3]}{[\text{NO}_x]} = \frac{\tau_{\text{NO}_x}}{\tau_{\text{HNO}_3}}$$

3. The mass balance equation for NO_x in the air parcel, following the initial injection, is

$$\frac{d[\text{NO}_x]}{dt} = \frac{[\text{HNO}_3]}{\tau_{\text{HNO}_3}} - \frac{[\text{NO}_x]}{\tau_{\text{NO}_x}}$$

Since NO_x and HNO_3 are conserved in the air parcel, $[\text{HNO}_3] = [\text{NO}_x]_0 - [\text{NO}_x]$. Substituting in the above equation,

$$\frac{d[\text{NO}_x]}{dt} = \frac{[\text{NO}_x]_0}{\tau_{\text{HNO}_3}} - \left(\frac{1}{\tau_{\text{NO}_x}} + \frac{1}{\tau_{\text{HNO}_3}} \right) [\text{NO}_x]$$

which is of the form

$$\frac{d[\text{NO}_x]}{dt} = P - k[\text{NO}_x]$$

where $P = [\text{NO}_x]_0/\tau_{\text{HNO}_3}$ and $k = (1/\tau_{\text{NO}_x} + 1/\tau_{\text{HNO}_3})$. The solution to this equation is

$$[\text{NO}_x] = [\text{NO}_x]_0 e^{-kt} + \frac{P}{k}(1 - e^{-kt})$$

so that $[\text{NO}_x]$ approaches steady state on a time scale $\tau = 1/k = (1/\tau_{\text{NO}_x} + 1/\tau_{\text{HNO}_3})^{-1}$. Since $[\text{HNO}_3] = [\text{NO}_x]_0 - [\text{NO}_x]$, $[\text{HNO}_3]$ approaches steady state on the same time scale. This is the desired result.

At 2 km, $\tau = (1/1.3) + (1/23) = 1.2$ days

At 10 km, $\tau = (1/6.6) + (1/19) = 4.9$ days

The time scale over which the HNO_3/NO_x concentration ratio approaches chemical steady state is shorter than the lifetime of the shortest species (NO_x). It is sufficiently short that one would in general expect to be close to chemical steady state.

4. The chemical steady state value of the HNO_3/NO_x concentration ratio increases rapidly with altitude, from $1.3/23 = 0.06$ mol/mol at 2 km to $6.6/19 = 0.35$ mol/mol at 10 km. As an air parcel initially at chemical steady state subsides, its HNO_3/NO_x concentration ratio will always be higher than the local chemical steady state value. Depending on the rate of subsidence, the departure from steady state may be large. As an extreme case, an air parcel brought down instantly from 10 km to 2 km would have a HNO_3/NO_x concentration ratio $0.35/0.06 = 6$ times higher than local chemical steady state.

5. Injection of fresh NO_x to the upper troposphere could take place by deep convection, lightning, or aircraft.

SOLUTIONS TO PROBLEMS, CHAPTER 12

12. 1 NO_x- and hydrocarbon-limited regimes for ozone production

1. The loss rate of NO_x from oxidation in the region is

$$L_{NO_x} = \frac{[NO_x]}{\tau_{NO_x}}$$

and the loss rate of NO_x from ventilation out of the region is

$$F_{NO_x} = \frac{U[NO_x]}{W}$$

where [NO_x] is the NO_x concentration in the region, $\tau_{NO_x} = 12$ hours is the lifetime of NO_x against oxidation, $U = 2 \text{ m s}^{-1}$ is the wind speed from the west, and $W = 1000 \text{ km}$ is the east-west dimension of the region. The fraction f of the NO_x removed by oxidation is

$$f = \frac{L_{NO_x}}{L_{NO_x} + F_{NO_x}} = \frac{1}{1 + \frac{\tau_{NO_x} U}{W}} = 0.92$$

Indeed most of the NO_x is oxidized within the region.

2. We must express the source of HO_x, $P_{HO_x} = 4 \times 10^6 \text{ molecules cm}^{-3} \text{ s}^{-1}$, and the emission of NO_x, $E_{NO_x} = 2 \times 10^{11} \text{ molecules cm}^{-2} \text{ s}^{-1}$, in the same units. Let us convert E_{NO_x} into a mean source of NO_x, P_{NO_x} , in the eastern United States box:

$$P_{NO_x} = E_{NO_x}(\text{area}/\text{volume}) = E_{NO_x}/h$$

where $h = 2 \text{ km}$ is the height of the box. Thus $P_{NO_x} = 1 \times 10^6 \text{ molecules cm}^{-3} \text{ s}^{-1} < P_{HO_x} = 4 \times 10^6 \text{ molecules cm}^{-3} \text{ s}^{-1}$.

Steady state for HO_x is defined by:

$$P_{HO_x} = L_{HO_x}(1) + L_{HO_x}(2) = L_{HO_x}(1) + fP_{NO_x}$$

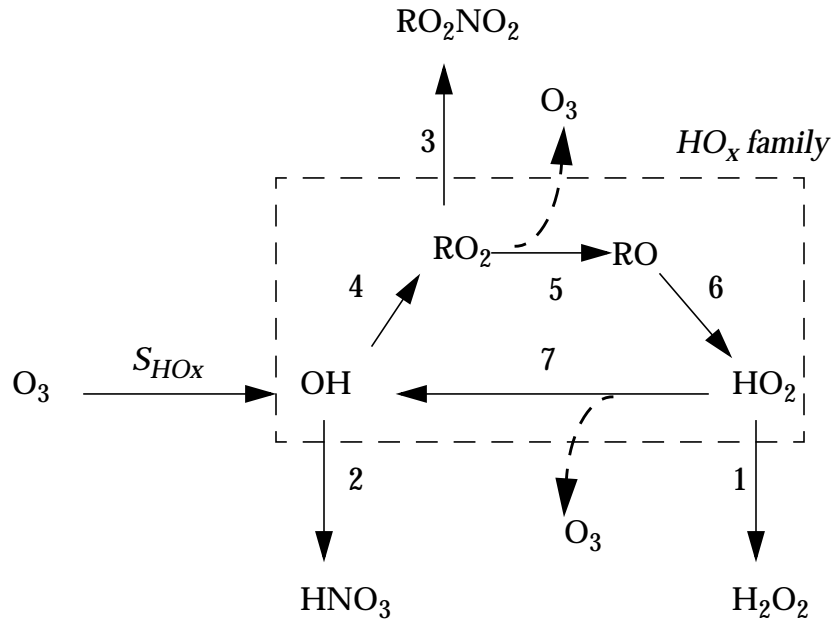
where $L_{HO_x}(1)$ and $L_{HO_x}(2)$ are the loss rates of HO_x by reactions (1) and (2), respectively; $L_{HO_x}(1) > L_{HO_x}(2)$ defines the NO_x-limited regime. Rearranging the above equation,

$$L_{HO_x}(1) = P_{HO_x} - fP_{NO_x} = 4 \times 10^6 - 9 \times 10^5 = 3.1 \times 10^6 \text{ molecules cm}^{-3} \text{ s}^{-1} > L_{HO_x}(2)$$

We conclude that O₃ production is NO_x-limited.

3.1. P_{HO_x} is less in October than in July because of the weaker radiation available for photolysis of O₃, which provides the principal source of HO_x.

3.2. In October $P_{HO_x} \approx fP_{NO_x}$; the source of HO_x is sufficiently weak that reaction (2) can provide the main sink of HO_x. Thus $L_{HO_x}(2) > L_{HO_x}(1)$ and O₃ production is hydrocarbon-limited.

4. Schematic for HO_x cycling:4.1. Ozone production rate $P_{O_3} = \text{rate}(5) + \text{rate}(7)$

Assume efficient cycling between HO_x species so that $\text{rate}(5) = \text{rate}(7)$ and therefore $P_{O_3} = 2\text{rate}(5) = 2k_5[\text{RO}_2][\text{NO}]$.

Use steady-state for HO_x to substitute for RO₂:

$$P_{\text{HO}_x} = L_{\text{HO}_x} \approx k_3[\text{RO}_2][\text{NO}_2][\text{M}]$$

since we assume that reaction (3) is the dominant loss process for HO_x. Replacing in above equation:

$$P_{O_3} = 2k_5 \left(\frac{P_{\text{HO}_x}}{k_3[\text{NO}_2][\text{M}]} \right) [\text{NO}]$$

4.2. If $[\text{NO}]/[\text{NO}_2]$ is constant, P_{O_3} is only a function of P_{HO_x} which depends on O₃, $h\nu$, and H₂O. Ozone production does not depend directly on either NO_x or hydrocarbons.

12. 2 Ozone titration in a fresh plume

1. Consider an elemental section of plume of thickness dx at a distance x from the source; the cross-sectional area of the plume is $A = \pi R^2/2 = \alpha^2 \pi x^2/2$ and its volume is $A dx$. Considering that NO_x is conserved in the plume and that air resides in the elemental section of plume for a time $dt = dx/U$, the

number of moles of NO_x in the elemental section is $Qdt = Qdx/U$. The concentration of NO_x is

$$[\text{NO}_x](x) = (\# \text{ moles } \text{NO}_x) / \text{volume} = 2Q / (\alpha^2 \pi x^2 U) \text{ in units of moles m}^{-3}$$

$$[\text{NO}_x](x) = 2Q / (\alpha^2 \pi x^2 U \beta) \text{ in units of ppb.}$$

2. If there were no ozone entrained in the plume, then all of the NO would remain NO as the plume advected downwind. The only process by which NO is converted to NO_2 is by reaction 1. As such, the concentration of ozone is the background concentration minus the amount destroyed in production of NO_2 , the latter term being equivalent to the concentration of NO_2 produced in the plume:

$$[\text{O}_3](x) = [\text{O}_3]b - [\text{NO}_2](x)$$

3.

$$[\text{O}_3](x) = [\text{O}_3]b - [\text{NO}_2](x) \quad (1)$$

$$[\text{NO}_2](x) + [\text{NO}](x) = \frac{2Q}{\pi \beta \alpha^2 x^2 U} \quad (2)$$

$$K = \frac{[\text{NO}](x)[\text{O}_3](x)}{[\text{NO}_2](x)} \quad (3)$$

Substitute eq. 3 into eq. 2:

$$[\text{NO}_2](x) + \frac{K([\text{NO}_2](x))}{[\text{O}_3](x)} = \frac{2Q}{\pi \beta \alpha^2 x^2 U}$$

Solve this for $[\text{NO}_2](x)$ and replace into eq. 1.

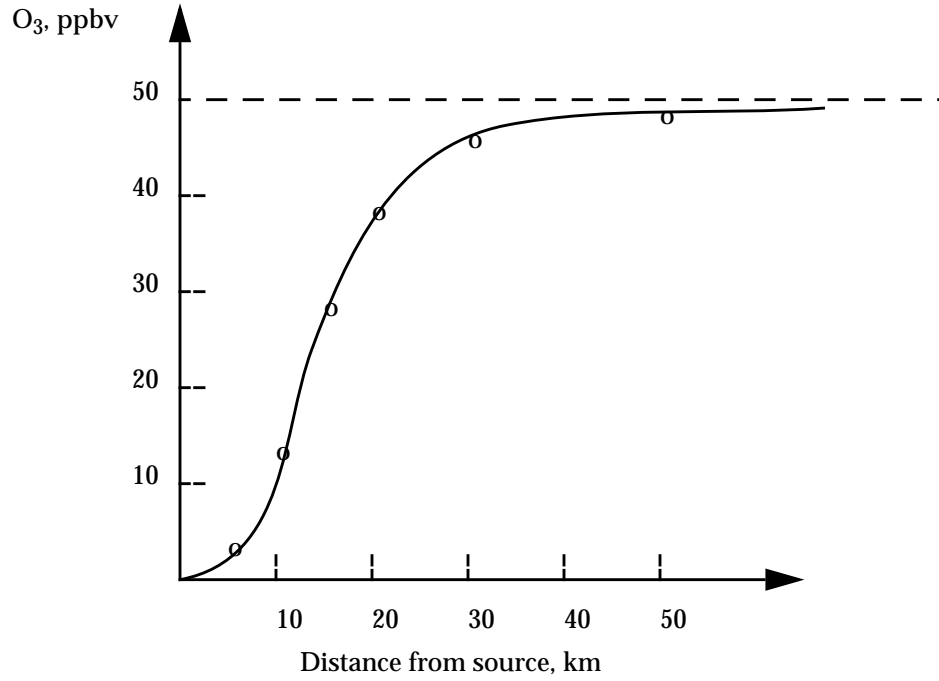
$$[\text{O}_3](x) = [\text{O}_3]b - \frac{\frac{2Q}{\pi U \beta \alpha^2 x^2}}{\left(1 + \frac{K}{[\text{O}_3](x)}\right)}$$

Solve this for $[\text{O}_3](x)$:

$$[\text{O}_3]^2(x) + [\text{O}_3](x) \left(K + \frac{2Q}{U \pi \beta \alpha^2 x^2} - [\text{O}_3]b \right) - K([\text{O}_3]b) = 0$$

$$[\text{O}_3](x) = \frac{-\left(K + \frac{2Q}{U \pi \beta \alpha^2 x^2} - [\text{O}_3]b \right) + \sqrt{\left(K + \frac{2Q}{U \pi \beta \alpha^2 x^2} - [\text{O}_3]b \right)^2 + 4K([\text{O}_3]b)}}{2}$$

Plot the result:



The ozone concentration in the plume recovers to 90% of background levels (i.e., 45 ppbv) at 30 km downwind of the source.

SOLUTIONS TO PROBLEMS, CHAPTER 13

13.1 Anthropogenic emissions and acid rain

1. The United States receives 1.3×10^9 moles per day of H^+ as HNO_3 from NO_x emissions and 2×10^9 moles per day of H^+ as H_2SO_4 from SO_2 emissions (H_2SO_4 releases two H^+). This totals $N = 3.3 \times 10^9$ moles per day of H^+ . We divide by the total volume V of water precipitating per day over the United States:

$$V = 1 \times 10^7 \text{ (km}^2\text{)} \times 2 \text{ (mm day}^{-1}\text{)} = 2 \times 10^{13} \text{ liters day}^{-1}$$

The mean H^+ concentration is therefore $[H^+] = N/V = 3.3 \times 10^9 / 2 \times 10^{13} = 1.7 \times 10^{-4} M$ and the corresponding pH is 3.8.

To get the concentration of H^+ we need to divide the latter figure by the total volume of water:

$$2 \times 10^{-6} \left(\frac{\text{km}}{\text{day}} \right) 1 \times 10^7 \text{ km}^2 = 2 \frac{\text{km}^3}{\text{day}} = 2 \times 10^{13} \frac{\text{L}}{\text{day}}$$

2. The actual pH range is 4.2 to 5.5; our simple calculation in question 1 overestimates $[H^+]$ because it does not take into account the presence of bases such as NH_3 and $CaCO_3$ which scavenge H^+ .

13.2 The true acidity of rain

Consider the electroneutrality equation for a rain sample analyzed in the lab :

$$\Sigma[Cat^+]_{lab} + [H^+]_{lab} = \Sigma[An^-]_{lab}$$

where $\Sigma[Cat^+]$ is the sum of concentrations of cations other than H^+ , $\Sigma[An^-]$ is the sum of concentrations of anions, and $[H]_{lab}$ corresponds to the pH of the sample measured in the lab: pH = 4.7, therefore $[H^+]_{lab} = 2.0 \times 10^{-5} M$. $HCOOH$ present originally in the rain has been consumed prior to analysis; we assume that all other cations (Cat^+) and anions (An^-) have been preserved. The true electroneutrality for the actual rain sample before $HCOOH$ has decayed is

$$\begin{aligned} \Sigma[Cat^+]_{lab} + [H^+]_{true} &= \Sigma[An^-]_{lab} + [HCOO^-] \\ \Rightarrow [H^+]_{true} &= [H^+]_{lab} + [HCOO^-] \\ \Rightarrow [H^+]_{true} &= [H^+]_{lab} + \frac{K_H K_1 P_{HCOOH}}{[H^+]_{true}} \\ \Rightarrow [H^+]_{true}^2 - [H^+]_{lab} [H^+]_{true} - K_H K_1 P_{HCOOH} &= 0 \end{aligned}$$

Solution to this quadratic equation yields $[H^+]_{true} = 3.8 \times 10^{-5} M$, or a true pH of 4.4. We find that $HCOOH$ accounts here for almost half of total rain acidity! However, it does no harm to ecosystems because it is rapidly consumed by microbes. From the perspective of damage to ecosystems, there is some rationale for measuring pH after $HCOOH$ has decayed.

13.3 Aqueous-phase oxidation of SO₂ by ozone

1. Reaction (1) consumes SO₃²⁻, thereby shifting equilibria (4) and (3) to the right and releasing H⁺.
2. Calculate the rate of sulfate production by reaction (1):

$$\begin{aligned}\frac{d[SO_4^{2-}]}{dt} &= k_1[SO_3^{2-}][O_3(aq)] \\ &= k_1 \frac{K_2 K_3 K_4 P_{SO_2}}{[H^+]^2} K_5 P_{O_3}\end{aligned}$$

Substituting numerical values, we find $d[SO_4^{2-}]/dt = 5.4 \times 10^{-9} \text{ M s}^{-1}$ or $4.7 \times 10^{-4} \text{ M day}^{-1}$ at pH 5, and 100 times less at pH 4. Starting from $[H^+] = 1 \times 10^{-5} \text{ M}$ at pH 5, significant acidity could be produced from the reaction over a time scale of several hours. However, the rate of acid production would decrease rapidly as $[H^+]$ increases, and is negligibly small at pH 4.

13.4 The acid fog problem

1. Steady state for SO₂:

$$\frac{E}{h} = (k_d + k_o)[SO_2]$$

where $h = 400 \text{ m}$ is the mixing depth (height of the box); E/h is the source of SO₂ per unit volume. Rearranging:

$$[SO_2] = \frac{E}{h(k_d + k_o)} \text{ (number density)} = \frac{E}{h(k_d + k_o)} \frac{P}{RT} \text{ (mixing ratio)}$$

Replacing numerical values yields $[SO_2] = 15 \text{ ppbv}$.

This level of pollution is below the EPA standards.

2. Since H₂SO₄ is incorporated immediately in the fog droplets, it is removed from the atmosphere at the same rate constant as the fog droplets. Steady state for H₂SO₄:

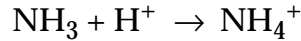
$$k_o[SO_2] = k_d[H_2SO_4]$$

Each H₂SO₄ molecule dissociates in the fog droplets to yield two H⁺ ions, so that the concentration $[H^+]$ in the fogwater (liquid water content L) is

$$[H^+] = \frac{2[H_2SO_4]}{L} = \frac{2k_o[SO_2]}{k_d L}$$

which gives a fogwater pH of 2.18.

3. NH_3 reacts to consume H^+ in a 1:1 stoichiometric ratio:



The source P_{H^+} of H^+ in the valley (in moles $\text{km}^{-2} \text{day}^{-1}$) is given by the emission of SO_2 (E_{SO_2}) times the fraction of that SO_2 that is oxidized to H_2SO_4 ($k_o/(k_o+k_d)$) times two (since each H_2SO_4 molecule releases two H^+ ions). We obtain $P_{\text{H}^+} = 4 \times 10^{12} \times (1/1.5) \times 2 = 5.3 \times 10^{12}$ moles $\text{km}^{-2} \text{day}^{-1}$. There is just enough NH_3 emitted to neutralize this acidity.

13.5 Acid rain: the pre-industrial atmosphere

1. Calculate the pH of rain at equilibrium with $P_{\text{CO}_2} = 280$ ppmv. The relevant equilibrium relationships are:

$$K_1 = \frac{[\text{CO}_2 \cdot \text{H}_2\text{O}]}{P_{\text{CO}_2}}$$

$$K_2 = \frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{CO}_2 \cdot \text{H}_2\text{O}]}$$

We also consider the charge balance equation:

$$[\text{H}^+] = [\text{HCO}_3^-] + [\text{OH}^-]$$

Since CO_2 is a weak acid, we can assume $[\text{H}^+] \gg [\text{OH}^-]$ and simplify the charge balance equation (this assumption will be verified at the end):

$$[\text{H}^+] = [\text{HCO}_3^-]$$

We thus have three equations for the three unknowns $[\text{H}^+]$, $[\text{CO}_2 \cdot \text{H}_2\text{O}]$, $[\text{HCO}_3^-]$; this leads to a unique solution for $[\text{H}^+]$ which we obtain by substitution:

$$[\text{H}^+] = (K_1 K_2 P_{\text{CO}_2})^{\frac{1}{2}}$$

Replacing numerical values yields $[\text{H}^+] = 2.1 \times 10^{-6}$ M, or $\text{pH} = 5.7$. The assumption $[\text{H}^+] \gg [\text{OH}^-]$ is verified.

2. Including the organic acids with $P_{\text{HCOOH}} = 0.1$ ppbv and $P_{\text{CH}_3\text{COOH}} = 0.1$ ppbv adds the equilibrium relationships:

$$K_3 K_4 = \frac{[\text{HCOO}^-][\text{H}^+]}{P_{\text{HCOOH}}}$$

$$K_5 K_6 = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{P_{\text{CH}_3\text{COOH}}}$$

and the charge balance equation is now:

$$[H^+] = [HCO_3^-] + [HCOO^-] + [CH_3COO^-]$$

Replacing the equilibrium relationships into the charge balance equation we obtain

$$[H^+] = (K_1 K_2 P_{CO_2} + K_3 K_4 P_{HCOOH} + K_5 K_6 P_{CH_3COOH})^{\frac{1}{2}}$$

Replacing numerical values for the individual terms on the right-hand side:

$$[H^+] = (4.6 \times 10^{-12} + 6.7 \times 10^{-11} + 1.5 \times 10^{-11})^{\frac{1}{2}}$$

we obtain $[H^+] = 9.3 \times 10^{-6}$ M, or pH = 5.0. Most of the acidity is contributed by formic acid (HCOOH).

3.1 The surface area of Earth = $4\pi(6400 \times 10^5 \text{ cm})^2 = 5.1 \times 10^{18} \text{ cm}^2$; so a global mean precipitation rate of 0.2 cm day⁻¹ corresponds to 3.7×10^{17} liters yr⁻¹.

$$[NO_3^-] = 1 \times 10^{12} \text{ moles yr}^{-1} / 3.7 \times 10^{17} \text{ liters yr}^{-1} = 2.7 \times 10^{-6} \text{ moles/liter}$$

$$[SO_4^{2-}] = 1 \times 10^{12} \text{ moles yr}^{-1} / 3.7 \times 10^{17} \text{ liters yr}^{-1} = 2.7 \times 10^{-6} \text{ moles/liter}$$

3.2 The charge balance equation is now

$$[H^+] = [HCO_3^-] + [HCOO^-] + [CH_3COO^-] + [NO_3^-] + 2[SO_4^{2-}]$$

Substitution yields a 2nd-degree equation for $[H^+]$:

$$[H^+]^2 - ([NO_3^-] + 2[SO_4^{2-}])[H^+] - (K_1 K_2 P_{CO_2} + K_3 K_4 P_{HCOOH} + K_5 K_6 P_{CH_3COOH}) = 0$$

Replacing numerical values:

$$[H^+]^2 - 8.1 \times 10^{-6} [H^+] - 8.7 \times 10^{-11} = 0$$

we obtain $[H^+] = 1.4 \times 10^{-5}$ M, or pH = 4.85. At that pH,

$$[HCOO^-] = \frac{K_3 K_4 P_{HCOOH}}{[H^+]} = 4.8 \times 10^{-6} \text{ M}$$

and hence $[HCOO^-] < 2 [SO_4^{2-}]$. Thus H₂SO₄ was the most important acid in the preindustrial atmosphere, followed closely by HCOOH.