AOSC 433/633 & CHEM 433/633 Atmospheric Chemistry and Climate

Problem Set #2 (150 points total) Due: Thurs, 21 Feb 2013 (start of class)

Late penalty: 10 points per day late, unless there is a legitimate medical or extra-curricular circumstance (i.e., band, athletics, GREs, etc) brought to our attention ***prior to the due date!***

Final deadline: Monday, 25 February, 6 pm: ***no credit*** will be given after final deadline.

Please "show your work", "carry units" while plugging numbers into equations, and express answers using a *reasonable* number of significant digits.

All three of us will be available on the afternoon of Wed, 20 Feb. However … ***please get started early!***

Information needed to complete this assignment is contained in the lecture notes and reading assignments. However it is fine to use any resource (book, website, etc) to complete this assignment provided the answers you provide reflect *your understanding of the solution*. While we encourage students to share notes and discuss course material, we also expect that problem set solutions reflect individual efforts. ***These questions are new for 2013 so archived notes from prior years are not likely to be helpful ☺***

1. Atmospheric Lifetimes (40 points total)

This problem can be completed using material presented as of Lecture 6

In **Lecture 6**, we noted that the lifetime for the removal of a chemical compound can be described as the burden divided by the loss rate: i.e.,

$$\tau = \frac{\text{Burden}}{\text{Loss Rate}}$$

a) (5 points) Given a volume mixing ratio for CH_4 of 1.8 parts per million and a mass of the atmosphere of 5.21×10^{21} gm, find the total atmospheric burden of CH_4, in units of terra gm (Tg).

Notes: 1 Tg = 10^{12} gm ; also, "burden" means "mass"

b) (10 points) The lifetime for removal of atmospheric CH_4 in the troposphere can be found from:

$$\tau_{\text{TROPOSPHERE}} = \frac{\text{Atmospheric Burden}}{\text{Tropospheric Loss Rate}}$$

and the lifetime for removal of atmospheric CH_4 in the stratosphere can be found from:

$$\tau_{\text{STRATOSPHERE}} = \frac{\text{Atmospheric Burden}}{\text{Stratospheric Loss Rate}}$$

Using the value for the atmospheric burden of CH_4 found in part a) and values of the tropospheric loss rate and stratospheric loss rate presented on the graph labeled "Sources and Sinks of CH_4" shown on Slide 8 of Lecture 6 (handout), calculate the lifetime for removal of atmospheric CH_4 in the troposphere and stratosphere.

Note: Atmospheric Burden appears in the numerator, rather than Stratospheric Burden or Tropospheric Burden, because we seek to know how long, on average, a particular molecule of CH_4 released to the <u>Atmosphere</u> will likely persist. Once air reaches the stratosphere, a particular molecule of CH_4 will have a greater chance of being removed, since there is so much less air in the stratosphere compared to the troposphere. However, the flow of air into the stratosphere is a slow process because mixing between tropospheric and stratospheric air masses is general restricted by the permanent temperature inversion that marks the tropopause. Since we are interested in the overall atmospheric lifetime of CH_4, we use the atmospheric burden in the numerator of both terms.

c) (10 points) If a compound is lost in the troposphere and in the stratosphere, the overall lifetime is given by:

$$\frac{1}{\tau_{\text{OVERALL}}} = \frac{1}{\tau_{\text{TROPOSPHERE}}} + \frac{1}{\tau_{\text{STRATOSPHERE}}}$$

Find the overall lifetime for CH_4.

d) (5 points) Compare the value for τ_{OVERALL} found in part c) to various values for the lifetime of CH_4 that have been discussed in class. Please comment on which of these agrees best with your calculation and which is furthest from your calculation.

e) (5 points) There are certainly instances where scientists would like to know how rapidly CH_4 is lost in the stratosphere, once air has crossed the tropopause. In this case, the appropriate equation is:

$$\tau'_{\text{STRATOSPHERE}} = \frac{\text{Stratospheric Burden}}{\text{Stratospheric Loss Rate}}$$

where the prime denotes this is a different stratospheric lifetime.

Provide an estimate of $\tau'_{\text{STRATOSPHERE}}$ for CH_4.

Note: To estimate the stratospheric burden of CH_4, you can multiply the atmospheric burden of CH_4 by the ratio of the mass of the stratosphere to the mass of the atmosphere.

Hint: Pressure is proportional to the mass per unit area of the overlying atmospheric column. Knowledge of surface pressure and tropopause pressure should allow for an estimate the appropriate ratio.

f) (5 points) Assume you set up an experiment for which you are able to follow two air masses, one located below the tropopause and one located above the tropopause. You devise a means to chemically tag a particular CH_4 molecule in each air mass.

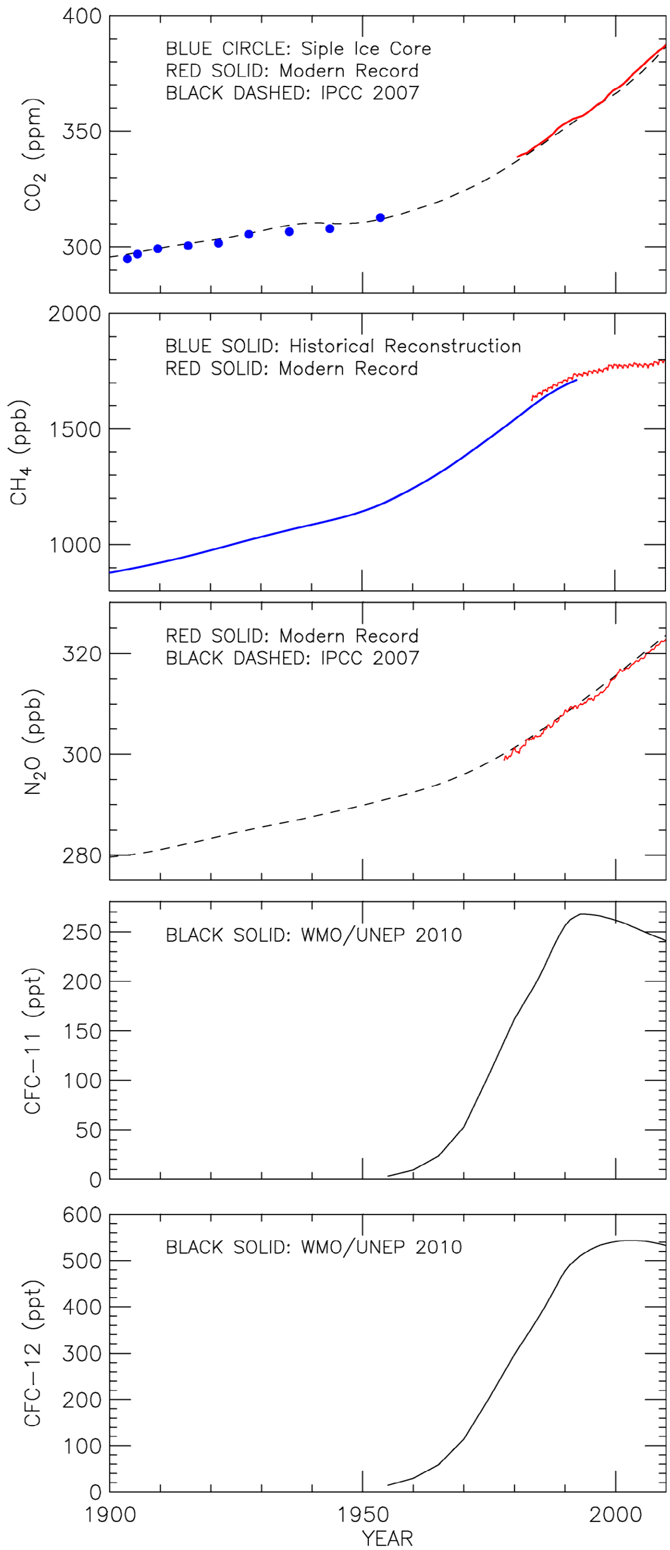
In which air mass will the tagged CH_4 molecule, on average, first decompose?

Hint: Some of the lifetime values found above should be worked into your reply.

2. Radiative Forcing from CO_2, CH_4, N_2O, CFC-11, and CFC-12 (70 points)

Most of this problem can be completed using material presented as of Lecture 7, but material from Lecture 8 could be helpful for answering part iv) of c & d.

The figure below shows time series of CO_2, CH_4, N_2O, CFC-11, and CFC-12 from 1900 to 2010.



a) (20 points) Find the change in radiative forcing (ΔRF) of the climate system, between years 1900 and 2005, due to CO_2, CH_4, N_2O, and halocarbons.

Notes: Sum the RF terms for CFC-11 and CFC-12 to obtain RF due to halocarbons.

There are two options for obtaining ΔRF due to CH_4 and N_2O.

Undergraduate students **may use a numerical evaluation of the formula that accounts for the overlap between CH_4 and N_2O absorption bands** ***or*** **may use the graphical representation of this formula from Lecture 7.**

Graduate students **must use a numerical evaluation of the formula. For numerical evaluation, consider using a computational tool such as Excel, MATLAB, FORTRAN, or IDL. However you solve the problem, please state the initial and final conditions for CH_4 and N_2O and the method used to calculate ΔRF.**

b) (10 points) A chart we have seen numerous times in class, including Slide 2 of Lecture 6 (handout), shows ΔRF of climate between 1750 and 2005, from the most recent IPCC report.

Compare and contrast your calculated values of ΔRF to those given by IPCC. Also, comment on whether it seems appropriate to compare your value of ΔRF found for 1900 to 2005, to the IPCC value that is based on 1750 to 2005.

c) (20 points) Sum the ΔRF you have calculated for CO_2, CH_4, N_2O, and halocarbons; then, add to this sum to the small contribution for ΔRF due to O_3 read off the IPCC chart. This quantity shall be called ΔRF_{GHG}.

The atmosphere undergoes external forcings due to processes other than GHGs. The most important other external forcing is due to release of aerosols, particulate matter resulting from the burning of fossil fuel and deforestation. The RF due to aerosols consists of two terms: the Direct effect and the Cloud albedo effect, also known as the Indirect effect.

Assume $\Delta RF_{AEROSOL\text{-}DIRECT}$ occurs at the IPCC best estimate, given by the blue bar on the chart.

i) Provide an estimate of the UPPER LIMIT for the *absolute value* of ΔRF from the Cloud Albedo Effect aerosol term shown in the IPCC chart due (i.e., the largest amount of aerosol cooling for this term). We shall refer to this term as $\Delta RF_{AEROSOL\text{-}CLOUD\text{-}ALBEDO}$.

ii) Using the value for $\Delta RF_{AEROSOL\text{-}CLOUD\text{-}ALBEDO}$ from part i), find the change in total RF due to all human activities, defined as:

$$\Delta RF_{HUMAN} = \Delta RF_{GHG} + \Delta RF_{AEROSOL\text{-}DIRECT} + \Delta RF_{AEROSOL\text{-}CLOUD\text{-}ALBEDO}$$

iii) Using the value for Earth's climate sensitivity parameter (λ from Lecture 4) from a climate model that represents the fact that a warmer atmosphere will hold more water, estimate the amount that globally averaged temperature should have risen, between 1900 and 2005, for the value of ΔRF_{HUMAN} found in part ii)

iv) Compare the value of ΔT found in part iii) to the actual rise in temperature between 1900 and 2005 *and* comment on whether climate feedback due to clouds and surface albedo would have to be either positive or negative to reconcile these two different values of ΔT.

d) (20 points) Repeat parts i), ii), iii), and iv) from above, using the LOWER LIMIT for the absolute value of ΔRF from the Cloud Albedo Effect aerosol term shown in the IPCC chart due (i.e., the smallest amount of aerosol cooling for this term).

3. The Greenhouse Effect (40 points)

This problem can be completed using material presented as of Lecture 7.

As shown in Figure 3.15 of Chemistry in Context, water vapor has minima in the transmittance at wave numbers of ~3750 cm^{-1} and ~1550 cm^{-1}.

a) (5 points) At what wavelengths, in units of μm, do these transmittance minima occur?

b) (5 points) For the two wavelengths found in part a), which is likely associated with a bending vibration and which is likely associated with stretching?

c) (5 points) What is the scientific importance of these two minima in the percent transmittance of water vapor: i.e., why do we care about these features of the water vapor IR spectrum?

d) (25 points) You have been brought in as a consultant for a chemical start up company, called *Green Chem*. The company is contemplating production of two new compounds. One of these compounds, code named ***Gas Green***, is unreactive with OH, is lost only by photolysis in the ultraviolet, and has a strong IR absorption feature at 830 cm^{-1}. The other compound, code named ***Substance Sunshine***, undergoes a moderately fast reaction with OH and has a strong IR absorption feature at 500 cm^{-1}.

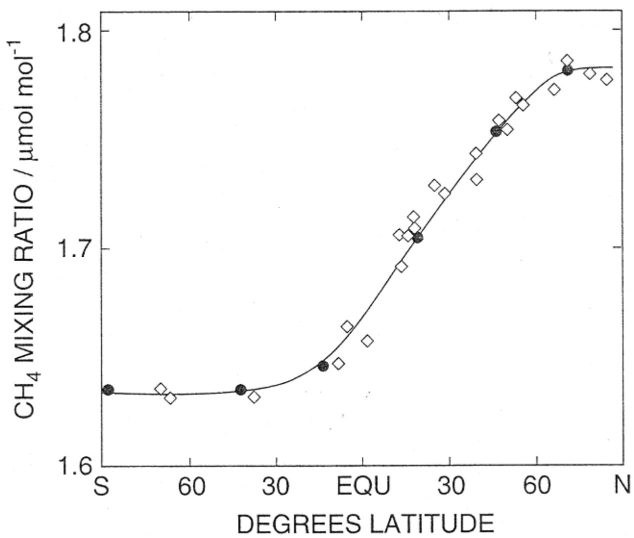
From an environmental perspective, which compound should the company pursue: ***Gas Green*** or ***Substance Sunshine*** ?

Of course, to receive full credit, you must provide an explanation for your answer ☺

4. Graduate Students Only (40 points)

This question is assigned ***only to the students*** enrolled in AOSC 633 or CHEM 633. If undergraduate students would like to work through the problem, they are welcome to do so. *But no extra credit will be given to undergraduates for solving this problem* ***!*** Sorry but if we were to give extra credit then the problem would no longer be exclusively assigned to graduate students ☺

The following figure was shown in **Lecture 6**:



Assume that:

- the lifetime for CH_4 is 9 years
- air in the NH is "well mixed" (rapid exchange, with a mean CH_4 mixing ratio of 1.80 ppmv) and air in the SH is also "well mixed" (mean CH_4 mixing ratio of 1.64 ppm)
- the time constant for exchange of air between the NH and the SH is 1 year
- CH_4 is in steady state for the NH and CH_4 is in steady state for the SH

Based on these assumptions:

a) find the NH source strength and the SH source strength, in Mt/year, for the emission of CH_4

b) sum these numbers and compare to the total, global CH_4 source strength given in class