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

Problem Set #1 (150 points total) Due: Tues, 12 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: Friday, 15 February, 5 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.

We will be present during office hours (Ross & Tim: Monday, 2:30 to 3:30 pm; Allison: Wed, 4 to 5 pm) and are happy to set up, via email, other times to meet).

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.

Please get started early!

1. Ozone Depletion Potential and Global Warming Potential (50 points total)

Note: you should be able to complete this question after Lecture 2

In Lecture 2, the formula for estimating ozone depletion potential (ODP) was given as:

\[
\text{ODP (species "i") = } \frac{\text{global loss of } O_3 \text{ due to continuous emission unit mass of "i"}}{\text{global loss of } O_3 \text{ due to continuous emission of unit mass of CFC-11}} 
\approx \left( \frac{\alpha n_{Br} + n_{Cl}}{3} \right) \frac{\tau_i}{\tau_{CFC-11}} \frac{MW_{CFC-11}}{MW_i}
\]

where:
- \( \tau \) is the global atmospheric lifetime
- \( MW \) is the molecular weight
- \( n \) is the number of chlorine or bromine atoms
- \( \alpha \) is the effectiveness of ozone loss by bromine relative to ozone loss by chlorine

Also in Lecture 2 the formula for estimating global warming potential (GWP) was given as:

\[
\text{GWP (Species)} = \frac{\int_{\text{time initial}}^{\text{time final}} a_{\text{Species}} \times [\text{Species (t)}] \, dt}{\int_{\text{time initial}}^{\text{time final}} a_{\text{CO2}} \times [\text{CO2 (t)}] \, dt}
\approx \frac{\int_{\text{time initial}}^{\text{time final}} [\text{Species (t)}] \, dt}{\int_{\text{time initial}}^{\text{time final}} [\text{CO2 (t)}] \, dt}
\]

where:
- \( a_{\text{Species}} \) = Radiative Efficiency (W m\(^{-2}\) kg\(^{-1}\)) due to an increase in Species
- \( a_{\text{CO2}} \) = Radiative Efficiency (W m\(^{-2}\) kg\(^{-1}\)) due to an increase in CO\(_2\)
- Species (t) = time-dependent response to an instantaneous release of a pulse of Species
- CO\(_2\) (t) = time-dependent response to an instantaneous release of a pulse of CO\(_2\)
Here we will examine the ODP and GWP of the compounds listed in the table below. It may be helpful to know that the chemical formula for CFC-11 is CCl₃F and its atmospheric lifetime is 45 years.

<table>
<thead>
<tr>
<th>Species</th>
<th>Chemical Formula</th>
<th>Lifetime (yrs)</th>
<th>Radiative Efficiency ($10^{-15}$ W m⁻² kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Dioxide</td>
<td>CO₂</td>
<td>---</td>
<td>1.79</td>
</tr>
<tr>
<td>Carbon Tetrachloride</td>
<td>CCl₄</td>
<td>26</td>
<td>4681</td>
</tr>
<tr>
<td>HCFC-124</td>
<td>C₂HClF₃</td>
<td>5.9</td>
<td>8943</td>
</tr>
<tr>
<td>HFC-23</td>
<td>CHF₃</td>
<td>270</td>
<td>15153</td>
</tr>
<tr>
<td>HFC-152a</td>
<td>C₂H₄F₂</td>
<td>1.4</td>
<td>7504</td>
</tr>
</tbody>
</table>

The formula for the response function of atmospheric CO₂ to an instantaneous release of a pulse of CO₂ was given in Lecture 2, Slide 9. Graphically, this response looks like:

![CO₂ Response Function](image)

a) (10 points) Calculate the ODP for Carbon Tetrachloride, HCFC-124, HFC-23.

b) (5 points) Is the effect of Carbon Tetrachloride on the ozone layer, on a per mass basis, larger or smaller than the effect of CFC-11 and why is the effect of Carbon Tetrachloride on the ozone layer either larger smaller than CFC-11?

c) (5 points) HCFC-124 was introduced by the Montreal Protocol to replace ozone depleting substances such as CFC-11, CFC-12, and Carbon Tetrachloride. Assuming the mass of HCFC-124 produced on an annual basis is the same as the combined mass of CFC-11, CFC-12, and carbon tetrachloride produced prior to the Montreal Protocol, was the introduction of HCFC-124 beneficial for the ozone layer?
d) (20 points) Calculate the GWP for Carbon Tetra., HCFC-124, HFC-23 over a 200 year time horizon.

Note: to complete this calculation, you will have to evaluate an integral to find the numerical value of the **numerator** of the GWP formula. Assume that the integrand of this integral is:

\[ [\text{Species } (t)] = e^{-t / \text{lifetime}} \]

that the limits of integration are 0 to 200 years, and that the initial abundance of each species is unity: i.e., \([\text{Species } (0)] = 1.0\) for all gases.

The numerical value of the integral that appears in the **denominator** of the GWP expression can be found either by coding up the CO₂ response function (given in lecture) within a numerical package or making an estimate from the graph given above (either method is perfectly fine).

e) (10 points) Without going through the math, although you are welcome to answer mathematically should you so desire, would it be better for Earth’s future climate to adapt HFC-152a as a longer term replacement for ozone depleting substances compared to HFC-23? If so, why? If not, why not?
2. Mixing Ratio and Number Density (50 points total)

Note: you should be able to complete this question after Lecture 3

The figures below show mass spectra (concentration as a function of molecular weight) of gaseous compounds, labeled A, B, C, D, and E obtained from a mysterious archive:
You have been given these spectra by a professor and asked to “make sense of the data” 😊

Please fill out the following table by:

a) (20 points) **calculating** the volume mixing ratio of each compound, using scientific notation (i.e., if a compound is present at 1.8 parts per million, write this as $1.8 \times 10^{-6}$), and write these values in the table below:

b) (15 points) **identifying** the chemical formula of each compound

<table>
<thead>
<tr>
<th>Identifier</th>
<th>Chemical Formula</th>
<th>Volume Mixing Ratio Mass Spectrum #1</th>
<th>Volume Mixing Ratio Mass Spectrum #2</th>
<th>Volume Mixing Ratio Mass Spectrum #3</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>B</td>
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<td></td>
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<td>C</td>
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<td>D</td>
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<tr>
<td>E</td>
<td></td>
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</tbody>
</table>
c) (15 points) Where were the various Mass Spectra acquired?

Mass Spectrum #1 _________________________________
Mass Spectrum #2 _________________________________
Mass Spectrum #3 _________________________________
3. Effective Temperature and Climate Change (50 points total)

Note: you should be able to complete this question after Lectures 4, using material from Lectures 2, 3, and 4.

a) (10 points) Compute the effective temperature Earth would have if there were no greenhouse gases (GHGs) present in the atmosphere, either natural or anthropogenic, for a mean albedo of 0.3.

b) (10 points) The actual temperature of Earth is considerably larger than the effective temperature found in part a), due to the radiative forcing (RF) of GHGs. The greenhouse gas that provides the most RF of climate is H$_2$O, the so-called natural GHG.

For the pre-industrial atmosphere: i.e., the atmosphere that existed in year 1900, the Earth’s mean effective temperature was 287 K.

Calculate the RF of climate ($\Delta$F from lecture 4) that was provided by H$_2$O and the ambient levels of CO$_2$, CH$_4$, N$_2$O, O$_3$, etc that existed in year 1900, needed to provide the effective, pre-industrial temperature of 287 K.

Carry out this calculation for an albedo of 0.3 and use the Earth’s climate sensitivity, parameter $\lambda$ from Lecture 4, found using a climate model that represents the fact that a warmer atmosphere can hold water.

c) (20 points) The graph below shows the influence of CO$_2$, CH$_4$, tropospheric O$_3$, halocarbons, and N$_2$O on the RF of climate, from 1900 to present.

i) How much would Earth’s surface temperature have risen, from 1900 to present, in response to this radiative forcing?

ii) How much did Earth’s mean surface temperature rise, from 1900 to present (or to year 2000, close enough to present for our purposes)?
iii) Compare the values found in part i) and ii): i.e., how does Earth’s “expected” rise in temperature due to RF of climate by GHGs compared to Earth’s “actual” rise in temperature.

Do the two values disagree at a level you consider to be significant?

If so, why might they disagree?

If not, comment on the meaning of the close agreement of these terms.
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 😊

a) (10 points) Calculate the mass of Earth’s atmosphere, in grams, by assuming:

Surface Pressure = 1013 mbar

and noting that:

Pressure = Force per unit area

Force = Mass × Acceleration

Note: the definition of millibar is given in MKS units on page 50 of the Jacobson reading. In class, we will generally use CGS units, although we often use “kilometer” to refer to altitude.

b) (10 points). Calculate the mass of carbon in Earth’s atmosphere in units of Giga tons (Gt), using only the C in CO₂ and assuming that CO₂ is uniformly distributed with a volume mixing ratio of 394 parts per million (ppm) throughout the world.

Here, we are using metric tons: 1 metric ton = 10³ kg; therefore, 1 Giga ton = 10¹⁵ grams.

c) (10 points). What fraction of the mass of carbon in Earth’s atmosphere is released each year by the burning of fossil fuels?

d) (10 points). Based on the Keeling curve shown in class and the fact that CO₂ exhibits little seasonal cycle in the SH, estimate how much mass of C, in units of Gt, is exchanged seasonally by the breathing of the biosphere? Compare this number to the annual increase of C in atmospheric CO₂ (again, in Gt). If we would somehow sequester all of the carbon released an annual basis by decay of biomass (i.e., collect all falling leaves and bury them), would this be a viable quantitative means to slow the rate of climate change?