AT 621, Fall 2012
Review for Exam 1

Write reaction rates and time rate of change of species concentrations.

Define lifetime; discuss types of sources and sinks

Set up a simple box model; deduce missing reservoir masses or fluxes

Describe coupled budgets

Describe oxidation state

Give examples of species (of various oxidation states) in the following biogeochemical cycles:
Carbon cycle, including ocean uptake and varied timescales
Sulfur cycle
Nitrogen cycle
Halogen cycle

Describe attenuation of radiation through the atmosphere. What wavelengths of solar radiation make it to the surface?

Describe the calculation of the photolysis rate constant (what data are needed, what it is sensitive to)

List important sources of OH

Describe the basic photochemical cycle

What is the PSSR?

What controls ozone production vs. destruction vs. neutral conditions?

Discuss how ozone changes seasonally as a function of altitude. What other factors contribute to variation in the ozone column year-to-year?

List the reactions comprising Chapman chemistry. Discuss the major limitations with the mechanism, as far as its ability to simulate observed stratospheric ozone.

Write a generalized catalytic cycle for ozone destruction, and name the species that can serve in this role. Give sources for each species.

What side reactions moderate the activity of catalytic cycles? Give some examples. How do family-family interactions come into play?

Why are Br and Cl together more effective at ozone destruction?

Compare the competing reactions:

$NO_2 + O \rightarrow NO + O_2$

$NO_2 + h\nu \rightarrow NO + O$

$NO_2 + O_3 \rightarrow NO_3 + O_2$

Discuss the elements that lead to the Antarctic ozone hole. What time of year is the hole observed? What conditions (that might vary year to year) favor the most dramatic ozone losses?

Discuss what Type I and Type II polar stratospheric clouds are (contrast composition and temperatures of formation).

Discuss ozone loss in the Arctic and at midlatitudes.

AT 621
Atmospheric Chemistry

Exam 1

Thursday,

October 11, 2007

Exam is 1 hour

FOUR PROBLEMS

** Note point weighting assigned to each problem **

CLOSED BOOK

CLOSED NOTES

1. *[20 points]*

Answer the following short questions / problems
(there are 4 TOTAL, each 5 points).

(a) Briefly describe (and explain) the global distribution of CO. Include an estimate of its lifetime, example sources and distributions of these, and most important sinks.

(b) Give examples of 3 species relevant to the nitrogen cycle. Arrange them from least to most oxidized.

(c) If a species has a lifetime ~1 week, how do you expect it to be distributed in the horizontal and vertical? Give an example of an atmospherically-relevant species that has such a lifetime / distribution.

(d) Give an example of one species that is distributed between the atmosphere and seawater. Why is this distribution important to atmospheric chemistry?

1. *[30 points]*

Carbonyl sulfide can undergo the following reactions:

	Reaction	Rate constant
1	$OCS + h\nu \rightarrow CO + S$	2.32×10^{-9}
2	$OCS + O \rightarrow CO + SO$	2.1×10^{-11}
3	$OCS + OH\cdot \rightarrow CO_2 + HS$	1.1×10^{-13}

Assume the average surface concentration (1000 mbar pressure) of OH· is 1×10^5 molecules cm^{-3} and that of O is 1×10^3 molecules cm^{-3}. Assume mixing ratios are constant throughout the atmosphere. Average tropospheric concentrations can be determined by assuming a mean pressure of 20 mbar in the stratosphere and 700 mbar in the troposphere.

All second-order rate constants have units of cm^3 $molecule^{-1}$ s^{-1}. The photolysis of OCS is shown to occur only for wavelengths shorter than 388 nm (Molina et al., 1981).

The average stratospheric mixing ratio of OCS is 380 ppt, while the global average tropospheric mixing ratio is 500 ppt. These mixing ratios correspond to averages of 4.75×10^8 molecules cm^{-3} in the stratosphere, and 6.25×10^9 molecules cm^{-3} in the troposphere. The volume of the stratosphere is 1.28×10^{25} cm^3 and of the troposphere, 7.62×10^{24} cm^3.

The molecular weight of sulfur is 32 g $mole^{-1}$. Avogadro's number is 6.022×10^{23} molecules $mole^{-1}$.

(a) Estimate the chemical lifetime of OCS in the troposphere.

(b) Estimate the chemical lifetime of OCS in the stratosphere.

(c) The sulfur fluxes needed to sustain the stratospheric aerosol layer are estimated to be $\sim 1 \times 10^{11}$ g(S) yr^{-1}. If all of the stratospheric OCS is converted to sulfate aerosol, with the reactions above being the rate-limiting steps, does OCS alone explain the source of stratospheric sulfate aerosol?

2. *[30 points]*

Consider the following sequence of reactions for the remote troposphere:

1 $O_3 + h\nu \rightarrow O_2 + O(^1D)$

2 $O(^1D) + H_2O \rightarrow 2OH\cdot$

3 $CO + OH\cdot \rightarrow CO_2 + HO_2\cdot$

Analyze the mechanism for the steady-state concentration of OH·. What does your result tell you about the factors influencing the oxidizing capacity of the troposphere?

3. [20 points]

Answer the following short questions
(there are 2 TOTAL, each 10 points).

(a) Write out the Chapman mechanism for stratospheric ozone production. Does it over- or under-estimate observed concentrations? Give an example of an additional reaction that must be considered.

(b) Explain BRIEFLY the sequence of events leading to rapid ozone depletion over the Antarctic.