

YOUR NAME: SOLUTIONS

AT 621
Atmospheric Chemistry

Exam 1

Thursday,
October 11, 2007

average 92.1
std dev 10.3

Approx letter grades:

> 97 A⁺
87-97 A
81-86 A⁻
75-80 B⁺
70-84 B

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).**

5 (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.

global distribution: global, with NH \rightarrow SH gradient (hemispheric)
lifetime: ~ months
sources: wild + prescribed fires (NH boreal, SH agri burning)
 anthrop. combustion (NA, Europe, Asia \rightarrow megacities)
sinks: OH reaction

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

[see notes] example

$$\begin{array}{c} \text{NH}_3 \\ \downarrow \\ \text{NO} \\ \downarrow \\ \text{HNO}_3 \end{array}$$

5 (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.

vertical: can mix to free troposphere
horiz: will remain in latitude band, could have some redistribution at least halfway around globe
example: aerosol

5

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

example : CO_2 (There are others, e.g. DMS)

This is imp. because uptake to oceans (or outgassing) is an important sink (or source) of CO_2 from the atmosphere (can elaborate more than this)

2. [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 $OH \cdot$ 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 $cm^3 \text{ molecule}^{-1} \text{ s}^{-1}$. 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 $1.28 \times 10^{25} \text{ cm}^3$ and of the troposphere, $7.62 \times 10^{24} \text{ cm}^3$.

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

- Estimate the chemical lifetime of OCS in the troposphere.
- Estimate the chemical lifetime of OCS in the stratosphere.
- The sulfur fluxes needed to sustain the stratospheric aerosol layer are estimated to be $\sim 1 \times 10^{11} \text{ g(S) yr}^{-1}$. 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?

(a) To get the chemical lifetime, we need to consider all sink reactions for OCS: $\tau = \frac{[\text{OCS}]_{\text{sr}}}{\sum \text{sinks}}$

In the troposphere we use $[\text{OCS}]_{\text{ss, trop}} = 500 \text{ ppt}$
 and sinks are rxns 2+3 (rxn 1 ^{probably} not active in trop)

$$r_2: k_2 [\text{OCS}]_{\text{ss}} [\text{O}] \quad k_2 = 2.1 \times 10^{-11} \frac{\text{cm}^3}{\text{molecule s}}$$

$$r_3: k_3 [\text{OCS}]_{\text{ss}} [\text{OH}] \quad k_3 = 1.1 \times 10^{-13} \frac{\text{cm}^3}{\text{molecule s}}$$

$$\tau = \frac{[\text{OCS}]_{\text{ss, trop}}}{[\text{OCS}]_{\text{ss, trop}} (k_2 [\text{O}] + k_3 [\text{OH}])}$$

avg pressure in trop; This scales conc.
 \downarrow

$$k_2 [\text{O}] = 2.1 \times 10^{-11} \frac{\text{cm}^3}{\text{molecules}} \left(1 \times 10^3 \frac{\text{molecules}}{\text{cm}^3} \right)_{\text{surface}} \cdot \frac{700 \text{ mbar}}{1013 \text{ mbar}}$$

$$k_3 [\text{OH}] = 1.1 \times 10^{-13} \frac{\text{cm}^3}{\text{molecule s}} \left(1 \times 10^5 \frac{\text{molecules}}{\text{cm}^3} \right)_{\text{surface}} \cdot \frac{700}{1013}$$

$$\tau = \frac{1}{\frac{1.45 \times 10^{-8}}{\text{s}} + \frac{7.6 \times 10^{-9}}{\text{s}}} = 4.52 \times 10^7 \text{ s} = 523 \text{ d} \approx \underline{1.43 \text{ yrs}}$$

(b) We make similar calculations for the stratosphere, but use given stratospheric average pressures to scale concentrations, AND include τ_1 in the sum of the sinks, since it is active in the strat:

$$\tau = \frac{[\text{OCS}]_{ss, \text{strat}}}{[\text{OCS}]_{ss, \text{strat}} (k_1 + k_2 [\text{O}] + k_3 [\text{OH}])}$$

$$k_1 = 2.3 \times 10^{-9} \text{ s}^{-1}$$

$$k_2 [\text{O}] = (2.1 \times 10^{-11}) \left(1 \times 10^8 \frac{\text{molec}}{\text{cm}^3}\right) \left(\frac{20 \text{ mbar}}{1013 \text{ mbar}}\right) \text{ s}^{-1}$$

$$k_3 [\text{OH}] = (1.1 \times 10^{-13}) \left(1 \times 10^5 \frac{\text{molec}}{\text{cm}^3}\right) \left(\frac{20}{1013}\right) \text{ s}^{-1}$$

$$\tau_{\text{strat}} = \frac{1}{2.3 \times 10^{-9} + 4.15 \times 10^{-10} + 2.07 \times 10^{-10}}$$

$$= 3.41 \times 10^8 \text{ s}$$

$$\tau_{\text{strat}} = \underline{10.8 \text{ year}}$$

(c) Need sulfur flux (OCS oxidation) $\geq 1 \times 10^{11} \text{ g(S) yr}^{-1}$
 Find total S production (= loss) rate from 3 relevant strat.

rxns.

We are told that $[\text{OCS}]$ averages $4.75 \times 10^8 \frac{\text{molec}}{\text{cm}^3}$ in strat

and total stratos. volume = $1.28 \times 10^{25} \text{ cm}^3$

so total # molecules = $4.75 \times 10^8 \frac{\text{molec}}{\text{cm}^3} \cdot 1.28 \times 10^{25} \text{ cm}^3$

$$= 6.08 \times 10^{33} \text{ molecules}$$

Problem 2 / 4

$$\begin{aligned} \text{total rate constant} &= 2.3 \times 10^{-9} + 4.15 \times 10^{-10} + 2.17 \times 10^{-10} \text{ s}^{-1} \\ &= 2.93 \times 10^{-9} \text{ s}^{-1} \end{aligned}$$

$$\begin{aligned} \text{total rate} &= (6.08 \times 10^{33} \text{ molecules}) (2.93 \times 10^{-9} \frac{1}{\text{s}}) \\ &= 1.78 \times 10^{25} \frac{\text{molecules}}{\text{s}} \end{aligned}$$

Each mole is 32 g

$$\text{total rate} = 1.78 \times 10^{25} \frac{\text{molecules}}{\text{s}} \cdot \frac{\text{mole}}{6.022 \times 10^{23} \text{ molecule mole}} \cdot \frac{32 \text{ g S}}{1 \text{ mole}}$$

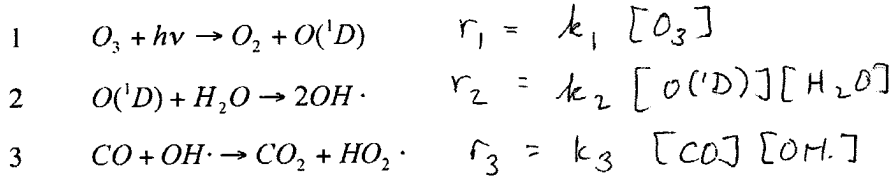
$$= 947 \frac{\text{g S}}{\text{sec}} \cdot \frac{3600 \text{ sec}}{\text{hr}} \cdot \frac{24 \text{ hr}}{\text{day}} \cdot \frac{365 \text{ d}}{\text{yr}} \cdot \frac{1 \text{ yr}}{10^{12} \text{ g S}}$$

$$= 2.99 \times 10^{-2} \frac{\text{Tg}}{\text{yr}}$$

$\sim 3 \times 10^{10} \frac{\text{g(S)}}{\text{yr}}$ about factor of 3-4 too small to account for all of the S production rate observed

3. [30 points]

Consider the following sequence of reactions for the remote troposphere:



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?

$$\begin{aligned}
 \frac{d[OH\cdot]}{dt} &= +2r_2 - r_3 && \text{since reactive} \\
 & && \downarrow \\
 &= 2k_2 [O(^1D)][H_2O] - k_3 [CO][OH\cdot] \approx 0 \\
 [OH\cdot] &= \frac{2k_2 [O(^1D)][H_2O]}{k_3 [CO]}
 \end{aligned}$$

Need to replace $[O(^1D)]$ too:

$$\begin{aligned}
 \frac{d[O(^1D)]}{dt} &= +r_1 - r_2 && \text{since reactive} \\
 & && \downarrow \\
 &= k_1 [O_3] - k_2 [O(^1D)][H_2O] \approx 0 \\
 [O(^1D)] &= \frac{k_1 [O_3]}{k_2 [H_2O]}
 \end{aligned}$$

$$[OH\cdot] = \frac{2 \cancel{k_2} [H_2O] \cancel{k_1} [O_3]}{k_3 [CO] \cancel{k_2} [H_2O]} = \frac{2 k_1 [O_3]}{k_3 [CO]}$$

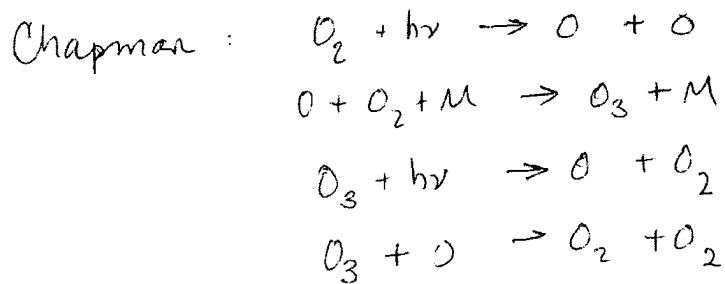
$[OH\cdot]$ created from $O_3 \Rightarrow$ should \uparrow where $O_3 \uparrow$
 main $[OH\cdot]$ loss via $CO \rightarrow$ may expect SM OH \uparrow
 Man NH?

Also k_1 photolysis \rightarrow tropics should have $\uparrow OH$

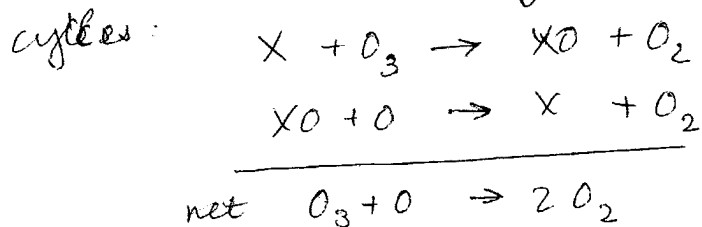
4. [20 points]

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.



it over estimates observed stratospheric O_3 concentrations because it is missing key catalytic destruction cycles:



where $\text{X} = \text{NO}, \text{H}, \text{Cl}, \dots$

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

- polar night + formation of vortex
 - isolates air chemically
 - radiates heat away → VERY cold

- PSCs form
 - heterogeneous chemistry converts Cl from inactive → active species
 - NO_x removal

- sunrise → photochem begins, rapid O_3 loss from Cl reactions until reservoirs rebuild

