CHEM. 250 – Spring, 2015
Exam 1 Key

Short Answer and Multiple Choice Section. Answers in bold

Answer the following two questions using the 4 **stratospheric** Chapman mechanism reactions:

a) $O_2 + h\nu \rightarrow 2O$
b) $O + O_2 + M \rightarrow O_3 + M$
c) $O_3 + h\nu \rightarrow O_2 + O$
d) $O + O_3 \rightarrow 2O_2$

1. Which reaction results in removal of harmful UV-C (220 to 280 nm) light and reduction of harmful UV-B (280 to 320 nm) light reaching the earth's surface? **c** (2 pts for b)

2. Catalysis of which reaction through mechanism I (with Cl, NO, or OH) leads to loss of ozone **d**

3. Which of the following conditions is a significant factor in the production of a stratospheric ozone hole?
a) the presense of polar stratospheric clouds
b) the removal of NO_x from the gas phase
c) the reactivation of Cl once the sun becomes present
d) all of the above

4. In the lower altitude polar stratosphere, in which way is chlorine most responsible for ozone destruction?
a) ozone destruction through a mechanism I type reaction
b) ozone destruction through a mechanism II type reaction (dimer forming intermediate)
c) activation of NO_x catalyzed ozone destruction
d) activation of HO_x catalyzed ozone destruction

5. Which compound initiates oxidation of alkanes in the **troposphere**?
a) OH b) HO_2 c) NO_2 d) O_3

6. Which of the following is the most significant source of NO in the **troposphere**?
a) oxidation of N_2O b) fuel N in the combustion of coal
c) thermal NO from high temperature fuel combustion
d) oxidation of NH_3

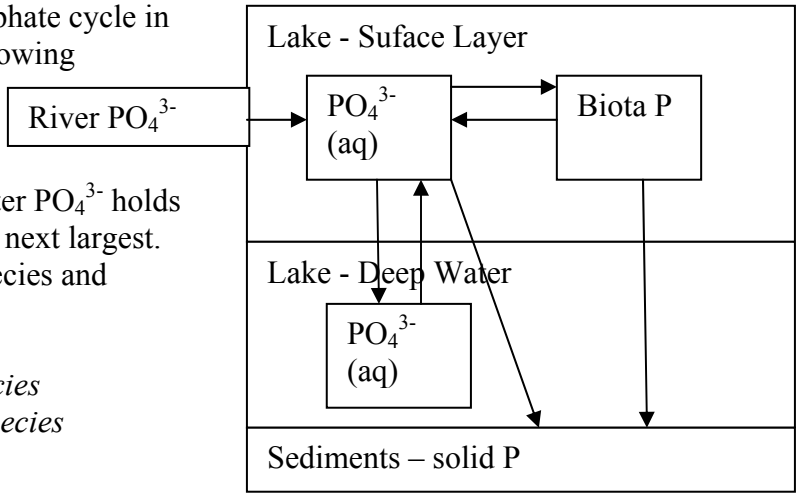
7. Which of the following is a significant primary pollutant?
a) CO b) O_3 c) HNO_3 d) H_2SO_4

8. The midwestern region of the US has higher sources of acid precursors (SO_2 and NO_x) than the northeastern region of the US. However, the northeastern region has seen more damage to its watersheds. Give one possible explanation for why this is:
_1) It takes time for acid to form so region with high deposition is downwind of regions of sources_2) The northeast has more susceptible soil types (granite vs. limestone)__

9. List one type of meteorological condition which contributes to photochemical smog episodes. Conditions: _1) inversions, 2) regional high pressure system, 3) high T_

Problem and Short Essay Question Section (be sure to show work if calculations are needed):

1. Using the diagram of the phosphate cycle in a lake to the right, answer the following questions.



a) In this particular lake, deep water PO_4^{3-} holds the most P, with biota P being the next largest. Which species is a "reservoir" species and which is "flux" species? (6 pts)

deep water PO_4^{3-} is reservoir species
surface water PO_4^{3-} is best flux species
Biota P o.k. as flux species

b) Biota P sinks to the bottom when the biota dies, which is the main P sink in the lake. If the average lifetime of the biota is 6 months, the lake biomass is 3.8×10^4 kg, and the %P of the biomass is about 0.5%, **calculate the biota P sink flux to sediments** in kg P/year. Asume the average lifetime is the turnover time. (8 pts)
$\tau = M/S$ where M = mass = $(3.8 \times 10^4$ kg)(0.005) = 190 kg P
and S = sink (flux)
so $S = M/\tau$ = 190 kg P/0.5 year = ***380 kg/year***

2. If the formation of reservoir species is ignored, NO_x can act as a catalyst for ozone destruction in the stratosphere by a mechanism I reaction. Write out the two reaction steps showing ozone destruction? (6 pts)

$NO + O_3 \rightarrow NO_2 + O_2$
$NO_2 + O \rightarrow NO + O_2$

bonus – from 2) Write one reaction which reduces NO_x's effectiveness in destroying ozone. This could be a reaction producing ozone or forming an inactive species. (3 pts)

1) $NO_2 + OH \rightarrow HNO_3$ – creates reservoir species in activating NO_x and HO_x
2) $NO_2 + ClO \rightarrow ClONO_3$ – creates reservoir species in activating NO_x and Cl
3) $NO_2 + h\nu \rightarrow NO + O$ – leads to ozone production

3. Give one Cl containing reservoir species that reactivates during ozone hole chemistry and explain (words or reactions) how Cl is reactivated. (8 pts)
a) $ClONO_2 + H_2O(in\ PSCs) \rightarrow HClO(PSCs) + HNO_3(PSCs)$
$HClO(PSCs) \rightarrow HClO(g) + h\nu \rightarrow OH + Cl$
b) $HCl + H_2O(in\ PSCs) \rightarrow Cl^-(PSCs) + H^+(PSCs)$
$Cl^- + HClO(PSCs) \rightarrow OH + Cl_2(g) + h\nu \rightarrow 2Cl$
PSC = polar stratospheric cloud

4. Describe NO_x's role in the production of tropospheric ozone by:
a) giving a two step reaction of an NO_x species forming ozone (6 pts) and

$NO_2 + h\nu \rightarrow NO + O$
$O + O_2 + M \rightarrow O_3 + M$

b) giving another reaction by which the NO_x product of the reaction in a) is recycled back to the NO_x reactant in step a) (without also destroying ozone). (4 pts)
$NO + HO_2 \rightarrow NO_2 + OH$
$NO + RO_2 \rightarrow NO_2 + RO$ *(reacts further with oxygen)*

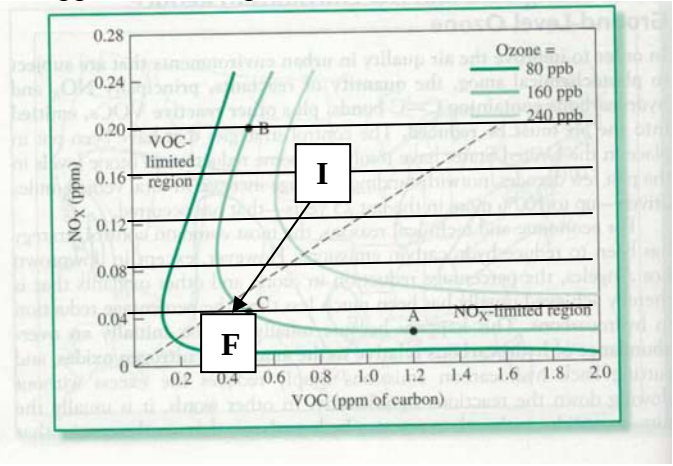
5. One way in which sulfuric acid is formed in the atmosphere is through gas phase reaction with OH.
a) Describe how this sulfuric acid ends up atmospheric aerosol particles and to what sized particles they add to the mass? (6 pts)

This produces $H_2SO_4(g)$ which can add to aerosol particle mass by 1) producing new particles or 2) adding to existing particles. The new particles formed are ultrafine while the addition to existing particles is mostly to accumulation or fine mode particles because these have the most surface area.

b) Does the size of the particles the sulfate ends up on affect the amount of haze? If so, what size causes the greatest decrease in visibility (per g of sulfate formed). (6 pts)

Yes. Production of accumulation mode (particles of the order of the wavelength of visible light produces the greatest decrease in visibility.

5. In an urban area in the Southesetern US, the total VOC (hydrocarbon) concentration is found to be 0.8 ppm C (1/2 anthropogenic and 1/2 natural) with NO_x concentrations of 0.16 ppm. Use the plot below to answer the following questions.



a) Based on the plot, which source should be reduced. Explain your answer. (4 pts)
See I on plot. It clearly is in the VOC limited region, so it makes the most sense to reduce hydrocarbons (pusing I to the lower ozone isopleths to the left).

b) The pollution plume drifts downwind and can be assumed to be diluted by a factor of 8 by background air (which has no NO_x but the same level of natural VOCs), show the new conditions on the plot. Is the limiting reactant the same or different? Explain your answer. (7 pts)
See arrow on plot to final region F. This is determined by decreasing NO_x by a factor of 8 (from 0.16 to 0.02 ppm). The anthropogenic VOC is also decreased by a factor of 8 from 0.4 ppm to 0.05 ppm. This is added to the natural 0.4 ppm VOC to get 0.45 ppm
It changed from VOC limiting to NO limiting due to the dilution (with natural VOC still present).

7. Determine the pH and aqueous NO_3^- concentration (in M) if air containing 1.0 ppbv HNO_3 enters a cloud with a pressure of 0.90 atm, a T of 293K, and a liquid water content (LWC) of 0.50 g H_2O (m air)$^{-3}$. Assume that 100% of the HNO_3 is scavenged and HNO_3 behaves as a strong acid. The density of water is 1.0 g mL^{-1}. (12 pts)
R = 0.0821 L atm mol^{-1} K^{-1}. 1000 L = 1 m^3.
Since 100% of is scavenged, we don't need to use Henry's law, but just convert from mol HNO_3/L air to mol HNO_3/L cloud. P_{HNO3} = (1.0 x 10^{-9} mole fraction)(0.90 atm)
n/V = P/RT = 9.0 x 10^{-10} atm/(0.0821 L atm/mol K)(293 K)
= (3.74 x 10^{-11} mol/L)(10^3 L/m^3) = 3.74 x 10^{-8} mol/m^3 air
[HNO_3] = (3.74 x 10^{-8} mol/m^3 air)(1/0.50 g H_2O (m air)$^{-3}$)(1.0 g/cm^3)(1000 cm^3/L) =
[HNO_3] = 7.5 x 10^{-5} M. Since it is a strong acid, we get H^+ and NO_3^- as products.
*So **[NO_3^-] = 7.5 x 10^{-5} M** and pH = -log(7.5 x 10^{-5}) = **4.13***