____Key___

ATOC 3500/CHEM 3151– Final Exam
Monday, May 7, 2018

There are eight questions on this exam worth a total of 100 points. If you are unsure of an answer, please provide additional information for possible partial credit.

1. (12 pts) True or False

___F__ (a) Nitrogen oxides act as bases in the atmosphere to increase the pH of rain. (they are acidic)

___T__ (b) Sulfuric acid and nitric acid are the two main contributors to the phenomenon known as "acid rain."

___T__ (c) A typical bimolecular reaction gets faster with increasing temperature.

___F__ (d) Although the ozone hole was first discovered in 1985, it wasn't until 2007 that observations showed it was caused by chlorine compounds. (1987)

___F__ (e) Coarse particles (diameters larger than 1 μm) are formed by fragmentation of even larger particles in collisions between particles in the atmosphere.

___T__ (f) There would be no ozone hole without the heterogeneous reaction of the long-lived reservoirs hydrochloric acid (HCl) and chlorine nitrate ($ClNO_3$).

___F__ (g) Isoprene, a compound emitted by trees, is important in the atmosphere because it has a long lifetime, and therefore is transported high into the stratosphere where it destroys ozone. (isoprene is short-lived)

___T__ (h) At any given time, the total amount of $O(^1D)$ in Earth's atmosphere is only about 1 gram. (Paul Monks video and class)

___F__ (i) Very little ultraviolet radiation reaches the earth's surface because UV is absorbed by nitrogen (N_2) in the stratosphere. (UV is absorbed by O_2 and O_3)

___T__ (j) The mixing ratio of O_2 at sea level is approximately 210,000 parts per million.

___F__ (k) The mixing ratio of O_2 at 5 km above sea level drops to about half of the value at sea level. (O_2 is relatively well mixed throughout the atmosphere)

___F__ (l) The Montreal Protocol, signed into international law in 1987 to protect the ozone layer, also prohibits the emissions of CO_2 that contribute to global warming. (nothing, yet, really prohibits CO_2 emissions)

2. (12 pts) Circle the letter that represents the best answer.

(A) Which of the following species can be a dominant oxidant in darkness?
- (a) OH
- (b) NO_3
- (c) O
- (d) fluorine
- (e) benzene

(B) Which of the following elements is found in at least 6 oxidation states in the atmosphere?
- (a) chlorine
- (b) hydrogen
- (c) sulfur
- (d) oxygen
- (e) all of the above

(C) What is a "Dobson Unit?"
- (a) a measure of the amount of ozone between the surface and top of the atmosphere.
- (b) the distance between two ice crystals in a cloud.
- (c) the temperature at which polar stratospheric clouds first form in the ozone hole.
- (d) a measure of the amount of visible light that passes through a cloud.
- (e) the weight of the smallest aerosol particle in a layer of haze.

(D) For a typical bimolecular reaction, the rate coefficient increases with _______.
- (a) pressure
- (b) temperature
- (c) humidity
- (d) all of the above
- (e) none of the above

(E) In the stratosphere, what is the primary source of ozone-destroying NO radicals?
- (a) photolysis of N_2O.
- (b) reaction of N_2O with $O(^1D)$
- (c) reaction of OH with N_2O_5.
- (d) a nuclear reaction between cosmic rays and carbon atoms in CO_2.
- (e) vertical transport of NO from the troposphere.

(F) What compound converts gaseous mercury into more toxic forms near the surface of sea ice in the polar regions in springtime?
- (a) SO_2
- (b) NO_2
- (c) I_2
- (d) CH_4
- (e) BrO

3. (12 pts) Short answers

(A) (3 pts) Suppose you know the concentration of ozone at an altitude of 20 km in units of molecules cm^{-3}. What quantity would you need to know to calculate the mixing ratio of ozone at 20 km, and describe how you could estimate P and T with sufficient accuracy (~30%) to derive this quantity without doing complicated calculations.

[M] (or "concentration" or "number density" of air).

P can be estimated using the barometric equation, with scale height of about 7 km.

We can estimate T or look at a temperature profile. 280 K is probably ok. Remember the stratosphere is warmer than the tropopause. But anything around 250 K to 300 K is a reasonable guess.

(B) (3 pts) A student who joined this class late is struggling to calculate the rate of the reaction below at the tropopause:

$$OH + NO_2 \rightarrow HNO_3$$

You know that the rate of the reaction is 2 $x10^7$ molecules cm^{-3} s^{-1} at sea level. Assuming that the mixing ratios of OH and NO_2 are the same at sea level and the tropopause, and that the pressure at the tropopause is 101.3 mbar, what is the rate of this reaction at the tropopause?

This was meant to make you think a little

Remember that whenever two radicals, A + B, recombine to form a stable compound, C, there needs to be a third body. So I wanted you to write the following:

$$\text{Rate} = k\,[OH]\,[NO_2]\,[M].$$

Then, I wanted you to note that a mixing ratio of X, fx, is "[X]/[M]", and substitute this back in:

$$\text{Rate} = k \text{ x } (f_{OH} \text{ x } [M]) \text{ x } (f_{NO2} \text{ x } [M]) \text{ x } [M].$$

So this means that termolecular reactions are really third order in [M]. That is, $[M]^3$. Since the pressure is 1/10 the pressure at sea level, this means the rate at 20 km is 1/1000 of the rate at sea level, or $2x10^4$ molecules cm^{-3} s^{-1}.

(C) (3 pts) The bimolecular reaction of HNO_3 with OH (followed by rapid photolysis of NO_3) is known to be a major source of NO_2 at the troposphere. Describe how you can calculate the concentration of HNO_3 at the tropopause if you know that NO_2 is in steady state and you know the both rate constant for the reaction of OH + HNO_3 and the concentration of OH (that is, [OH]). Base your result on the answer you obtained for the rate of the OH + NO_2 reaction that you found in Part (B).

We expect the rate of loss of NOx from part (B) (in this case, 2×10^4 molecules cm^{-3} s^{-1} , but could be whatever value you got) to be equal to the rate of formation of NOx, or k_2 [OH] [HNO_3].

$$\text{So } k_2 [OH] [HNO_3] = \text{“Rate”}$$

Or, for my answer to Part (B)

$$k_2 [OH] [HNO_3] = 2 \times 10^4 \text{ molecules cm}^{-3} \text{ s}^{-1}$$

$$[HNO_3] = 2 \times 10^4 \text{ molecules cm}^{-3} \text{ s}^{-1} / (k_2 [OH])$$

(D) (3 pts) You are a passenger on an airplane that is descending into a city that is known to be highly polluted. The airplane can land only if the visibility is greater than 10 km. The pilot makes an announcement that she has been unable to communicate with the control tower for the past 4 hours, so she is reluctant to descend. However, she says that she has a recent reading of particulate matter at the airport, and she wonders if anyone on the plane can confirm whether it will be safe to land. What is the maximum value of $PM_{2.5}$, in μg m^{-3}, that is allowable in order for a safe landing? Explain your answer.

We know that the product of PM and visibility is 1000, so if visibility needs to be greater than 10 km, the PM must be less than 100 μg m^{-3}. This is a tall order for many heavily polluted cities – some have values above 500 μg m^{-3}. Not to scare anyone, but just think the next time you land in a city that is known for bad air quality. It means the pilots are working very hard to land the plane using instruments – they probably can't see the end of the runway.

4. (9 pts) The pH of pure water is 7 (meaning that $[H^+] = 10^{-7}$).

(A) (2 pts) What is the typical pH of rain that falls in a 'clean' environment?

5.6

(B) (4 pts) What naturally occurring gas in the atmosphere increases the acidity of rain in this 'clean' environment, and write the pair of equilibria that can be used to calculate the pH of water in equilibrium with this gas.

Carbon dioxide

$$CO_2 + H_2O \rightarrow H_2CO_3$$
$$H_2CO_3 \rightarrow H+ + HCO_3^-$$

(C) (3 pts) What human-produced pollutants are most responsible for further increasing the acidity of rain?

Sulfuric acid and nitric acid (H_2SO_4 and HNO_3)

5. (10 pts) Assessing the Importance of Heterogeneous Chemistry of PAN

To understand the impact of submicron particles on atmospheric chemistry, we can calculate the rate of a heterogeneous reaction of a compound "X" on those particles. One compound that is an important reservoir for reactive nitrogen is called peroxyacetyl nitrate, or "PAN". PAN can react rapidly with water condensed on aerosol particles and cloud droplets. Note: The use of the subscripts "gas" and "aerosol" below mean the compounds are in the gas and particle phases, respectively.

$$PAN_{gas} + H_2O_{aerosol} \rightarrow HNO_{3\ aerosol} + CH_3COOH_{gas}$$

(a) (4 points) In addition to the concentration of PAN, what other quantities would you need to know in order to estimate a heterogeneous reaction rate for this process (i.e., d[PAN]/dt = "rate of reaction")

Velocity of PAN, surface area density of particulate (i.e., of the H_2O aerosol), and reactivity (or "sticking") coefficient. Note – [H_2O] isn't specific. This usually means the concentration of water vapor, and this isn't a gas-phase reaction.

(b) (3 points) Show how the lifetime of PAN with respect to the heterogeneous reaction on water aerosols is independent of the concentration of PAN.

Lifetime of PAN = [PAN]/(1/4 g v [SA] [PAN])
= 4 / (g v [SA])

(c) (3 pts) Assume you know the rate of the heterogeneous reaction of PAN. What other two processes would you need to consider in order to assess whether or not the heterogeneous reaction of PAN is important in the atmosphere?

Photolysis and reactions with oxidants like OH, O_3, etc.. PAN is also a weakly bound molecule, and it tends to decompose when it gets warm. So we might want to look at temperatures too. But the key here is that for the heterogeneous reaction to be important, it has to be faster than the other typical processes that occur..

6. (13 pts) Scientists have designed a hypothetical new chemical compound, CH_2FCl, called "OzoneSafe" to be used as a replacement for chlorofluorocarbons in air conditioners and spray cans. They expect the compound to react with the OH radical in the troposphere as follows:

$$CH_2FCl + OH \rightarrow CHFCl + H_2O \qquad k = 1x10^{-13}\ cm^3\ molecule^{-1}\ s^{-1}$$

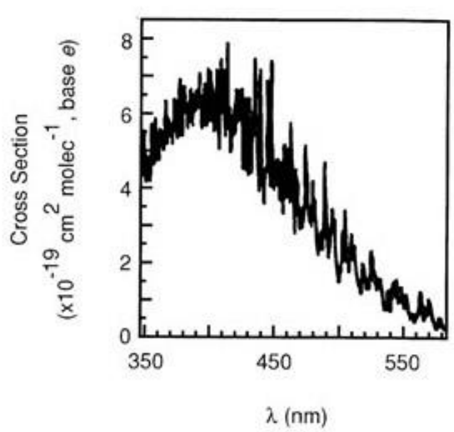
(a) (4 pts) What must the concentration of OH be if the lifetime of OzoneSafe with respect to reaction with OH is 10^7 seconds?

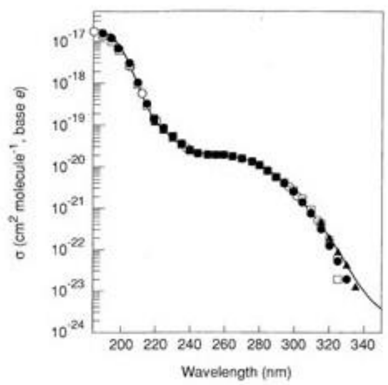
The product of the rate constant and the concentration of OH is $1/10^7$, so OH must be $1x10^6$ molecules cm^{-3}.

(b) (4 pts) 10^7 seconds is 116 days. Explain why OzoneSafe, despite containing a chlorine atom that is known to destroy ozone, would not considered hazardous for the stratospheric ozone layer.

In 116 days, this lifetime is too short for the molecules to reach the stratosphere and release their constituent chlorine atoms that would destroy ozone. So they just don't get the chance to destroy ozone.

(c) (5 pts) There is another hypothetical compound called "EvenMoreOzoneSafe" (or EMOS for short), with the chemical formula $CHFCl_2$. EMOS is expected to NOT react with OH, O_3, or NO_3. In addition, EMOS is not soluble in water. Which of the following two absorption spectra below (left or right) is most likely that of EMOS, and why?





Answer: Left. In order to be even more "ozone safe" than OzoneSafe, EMOS must be destroyed even faster in the troposphere than OzoneSafe, which has a lifetime of 116 days. But EMOS doesn't appear to react with OH, O3, or NO3, and it isn't water soluble. So it won't rain out. So it must photolyze in the troposphere. The molecule on the left has a significant cross section in the visible, whereas the one on the right absorbs very little light beyond 300 nm. So it must be the one on the left.

7. (19 pts) One of the consequences of the short tropospheric lifetime of "OzoneSafe" from Problem 6, is that it contributes to air pollution. In the reaction scheme below, fill in the missing molecules/species, indicated by underlined spaces. Hint: Use Problem 20 as a guide.

(A) (5 pts) Fill out the appropriate "Rate" term on the right of each reaction, using symbols (i.e., k or J for the rate coefficient and concentrations).

$CH_2FCl + OH \rightarrow CHFCl + H_2O$	Rate 1 = k_1 [CH2FCl] [OH]
$CHFCl + O_2 + M \rightarrow$ _$CHFClO_2$_ + M	Rate 2 = k_2 [CHFCl] [O_2][M]
$CHFClO_2$_ + NO → _CHFClO_ + NO_2	Rate 3 = k_3 [$CHFClO_2$] [NO]
$CHFClO + O_2 \rightarrow CFClO$ + _HO_2_	Rate 4 = k_4 [CHFClO] [O_2]
_HO_2 + NO → OH + _NO_2_	Rate 5 = k_5 [HO_2] [NO]_
_NO_2_ + hν → O + _NO_	Rate 6 = J_6 [NO_2]_
O + _O_2_ + M → O_3 + M	Rate 7 = k_7 [O] [O_2] [M]

(B) (3 pts) Assuming that reactions 5 and 6 are in steady state, write an expression for the ratio of [NO]/[NO_2].

$$k_5 [HO_2] [NO] = J_6 [NO_2]$$

$$\text{so } [NO] / [NO_2] = J_6 / (k_5 [HO_2])$$

(C) (2 pts) In the reaction scheme above, we call OH a catalyst. What do we mean by the term "catalyst?"

It facilitates the reaction, but is not consumed in the process.

(D) (3 pts) What two reactions in the troposphere are primarily responsible for the production of OH?

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

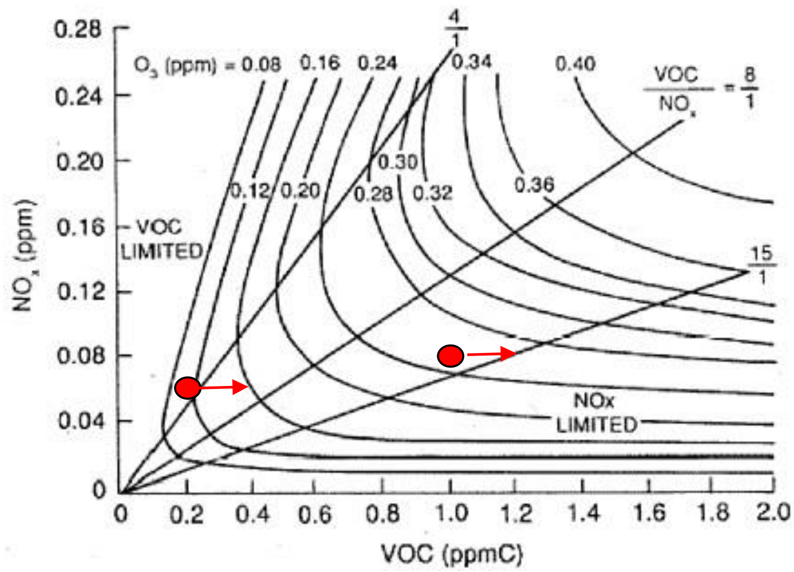
$$O(^1D) + H_2O \rightarrow OH + OH$$

(E) (2 pts) Explain why the steady rise of the atmospheric abundance of CH_4 (methane) is likely to contribute to an increase in the lifetimes of many compounds in Earth's atmosphere, including our hypothetical "OzoneSafe."

$$CH_4 + OH \rightarrow CH_3 + H_2O$$

Lifetimes of many species are inversely proportional to [OH]. So as CH4 increases, and OH decreases, the lifetimes will increase.

(F) (4 pts) Using the figure below (an example of the Empirical Kinetics Modeling Approach, or EKMA), describe how emissions of "OzoneSafe" (a volatile organic compound) will impact tropospheric ozone production differently in a rural area like the Utah desert, where NOx = 0.06 ppm and VOC = 0.2 ppm, than in an urban area where NOx = 0.08 ppm and VOC = 1.0 ppm.



Answer: (hint - It might be helpful to draw on the figure).

See dots (for NOx and VOC abundances in the rural and urban settings) and arrows (indicating the direction of a change in VOCs, such as an emission of "OzoneSafe"). Note that the dot at the left "sees" a larger gradient – that is, for a given emission of VOC, there is a larger increase in ozone than for the point on the right. So this shows that emissions of VOCs are more effective of producing ozone in a clean rural setting than in a environment that is already polluted.

8. (13 pts) The discovery and explanation for the ozone hole over Antarctica had major implications for our understanding of the role of human activities in global environmental problems. As a result, many of the lessons learned in dealing with the ozone hole have carried over into other areas of environmental research and policy.

(a) (2 pts) What class of compounds emitted by human activities at the surface is responsible for the ozone hole?

Chlorofluorocarbons (CFCs)

(b) (3 pts) During what time of the year (i.e. season, or month(s)) does the Antarctic ozone hole occur, and what processes, specifically, occur in the 2-3 months leading up to the ozone hole that are important for setting up the conditions necessary for radicals to rapidly destroy ozone?

The ozone hole forms at the end of winter, in early springtime. August/September is when most of the ozone is destroyed. Leading up to this, temperatures decrease, the circumpolar winds ("vortex") strengthens, polar stratospheric clouds form, and heterogeneous reactions convert benign forms of chlorine into reactive forms.

(c) (3 pts) Give an example of a catalytic cycle that occurs in the ozone hole that involves the main reactive radical formed when the source chemicals in Part (a) break down in the stratosphere. Note – DON'T use oxygen atoms in your cycle because O_2 photolysis is insignificant in the lower stratosphere during the time of year that the ozone hole occurs.

$$ClO + ClO + M \rightarrow Cl_2O_2 + M$$
$$Cl_2O_2 + h\nu \rightarrow Cl + Cl + O_2$$
$$Cl + O_3 \rightarrow ClO + O_2$$

(d) (2 pts) About how long does it take for all of the ozone in the layer ~16-24 km above the surface to disappear during an "ozone hole?"

Just one month.

(e) (3 pts) List a heterogeneous reaction that converts benign (i.e., non-ozone depleting) compounds into the highly reactive form of chlorine that is responsible for the ozone hole. What atmospheric constituents are responsible for producing the particles that provide the surface area for this heterogeneous reaction?

$$HCl + ClNO_3 \rightarrow Cl_2 + HNO_3$$

Nitric acid and water are responsible for forming stratospheric clouds.