ATOC 3500/CHEM 3151 – Final Exam
Wednesday, May 4, 2011, 4:30-7:00 pm

You will not need a calculator for this exam. If you are unsure of an answer, please provide additional information for possible partial credit.

1. (16 pts) Multiple choice (pick the best answer)

(i) (2 pts) What is the term that refers to the removal of gases and particles on Earth's surface by a direct transfer process that does not involve precipitation.
(a) Rainout
(b) Fallout
(c) Photolysis
(d) Dry deposition
(e) All the above

(ii) (2 pts) The "mixing ratio by volume" is identical to what quantity used commonly by chemists?
(a) concentration
(b) pH
(c) mole fraction
(d) partial pressure
(e) molecular weight

(iii) (2pts) If all the ozone in the atmosphere were collected, separated from air, and compressed to sea-level pressure (1 atm), it would occupy a layer how deep?
(a) 3 millimeters
(b) 3 meters
(c) 300 meters
(d) 3 km
(e) 30 km

(iv)(2 pts) Where are the largest ozone columns found?
(a) At high northern latitudes (60^o-90^o N) in springtime (February-April)
(b) At the south pole in springtime (September-November)
(c) In the tropics (30^o S to 30^o N) in winter (January-February)
(d) At the north pole in autumn (October-December)
(e) None of the above – ozone columns do not vary with location or season.

(v) (2 pts) Which of the following quantities is not a major factor for photolysis of a molecule?
(a) the absorption cross section
(b) the energy of the molecular bond that is being broken
(c) the output of the sun (solar spectrum)
(d) the time of day (position of sun in the sky)
(e) temperature and pressure

(vi) (2 pts) The central feature of perturbed chemistry of the polar stratosphere is the conversion of what two important reservoirs of gas-phase chlorine into the more photolytically active form Cl_2?
(a) $ClONO_2$ and ClNO
(b) HCl and $ClONO_2$
(c) Cl and ClO
(d) ClNO and HOCl
(e) ClOCl and OClO

(vii) (2 pts) Which of the following was not observed when the NASA ER-2 aircraft flew into the ozone hole in September 1987?
(a) Abundances of nitrogen oxides (NO_y) were significantly smaller than those outside the ozone hole.
(b) Abundances of O_2 were significantly smaller than those outside the ozone hole.
(c) Abundances of H_2O were significantly smaller than those outside the ozone hole.
(d) Ozone abundances were less than half of those outside the ozone hole.
(e) ClO abundances were nearly 10 times larger those outside the ozone hole.

(viii) (2 pts) Which of the following is not an important ozone-destroying free radical?
(a) chlorine (Cl)
(b) bromine (Br)
(c) fluorine (F)
(d) hydroperoxy (HO_2)
(e) nitric oxide (NO)

2. (12 pts) In order for a chemical compound to have a significant impact on ozone in the stratosphere, it must either be injected directly in the stratosphere (e.g., explosive volcano, rocket, or aircraft) or live long enough to mix throughout the atmosphere.

(a) (2 pts) What physical characteristic of the upper atmosphere inhibits vertical mixing of air from the troposphere to the stratosphere?

Temperature (there is an inversion – air gets warmer at higher altitudes)

(b) (2 pts) How does stratospheric ozone contribute to this physical characteristic?

Ozone absorbs sunlight, which deposits heat into the stratosphere.

(c) (2 pts) How is ozone formed in the stratosphere?

Photolysis of O_2 to form oxygen atoms, followed by the three-body recombination reaction $O + O_2 + M \rightarrow O_3 + M$

(d) (2 pts) Although the ozone bond is weak enough to be broken by a photon in the visible or near infrared portion of the spectrum, ozone is only photolyzed in the ultraviolet. Where does this excess energy absorbed by the ozone molecule go?

It produces O and O_2 fragments with excess internal energy (homework problem 8). This makes these fragments very reactive (it is the source of $O(^1D)$ that ultimately makes OH by reacting with water and NO by reacting with N_2O).

(e) (4 pts) Nobel Paul Crutzen first proposed that bacteria at Earth's surface are responsible for ozone destruction in the stratosphere. Name a molecule produced by bacteria that can lead to ozone destruction, and describe the basic steps that are necessary for that destruction to occur.

N_2O (nitrous oxide) and CH_4 (methane) are produced by anaerobic processes, and these are long-lived in the troposphere, so they can mix throughout the atmosphere and eventually reach the stratosphere. N_2O breaks down into NO, which is a catalyst for ozone destruction. CH_4 oxidizes into H_2O, which is a source of OH, also a catalyst.

$$X + O_3 \rightarrow XO + O_2$$
$$XO + O \rightarrow X + O_2$$

3. (15 points) Bromine is considered to be a very potent destroyer of ozone both in the stratosphere and near the surface in both polar regions (Arctic and Antarctic). The following mechanism is known to cause ozone destruction:

$$BrO + ClO \rightarrow Br + Cl + O_2 \qquad k_1$$

$$Br + O_3 \rightarrow BrO + O_2 \qquad k_2$$

$$Cl + O_3 \rightarrow ClO + O_2 \qquad k_3$$

(a) (2 pts) Is this a "catalytic cycle"? Why or why not?

Yes – both Br and Cl are recycled into BrO and ClO, so the net reaction which destroys ozone is catalytic – Br/BrO and Cl/ClO are required for the reaction, but they are not consumed in the process.

(b) (3 pts) Write a rate expression for the change of ozone with time ($-d[O_3]/dt$) based on reactions (2) and (3).

$$-d[O_3]/dt = Rate2 + Rate3 = k_2[Br][O_3] + k_3[Cl][O_3]$$

(c) (3 pts) Write a steady-state expression for [Br] and a steady-state expression for [Cl], and show how these can be substituted into your answer for Part (b) to express the ozone loss rate in terms of reaction (1) only.

$$-d[Br]/dt = Rate2 - Rate1 = k_2[Br][O_3] + k_1[BrO][ClO] = 0$$

$$-d[Cl]/dt = Rate3 - Rate1 = k_3[Cl][O_3] + k_1[BrO][ClO] = 0$$

Substituting into (b),

$$-d[O_3]/dt = Rate2 + Rate3 = Rate\ 1 + Rate\ 1 = 2k_1[BrO][ClO]$$

Note, this is the expression you used to calculate ozone loss in homework 14.

(d) (3 pts) Based on your answer to Part (c), write an expression for the lifetime of ozone.

$$\text{Lifetime of } O_3 = [O_3]/(\text{rate of loss}) = [O_3] / 2k_1[BrO][ClO]$$

(e) (2 pts) As a graduate student, Prof. Toohey published a paper showing that the reaction between ClO and BrO also forms BrCl (see reaction (4) below). Explain why reaction (1) above can lead to ozone destruction in darkness, whereas if reaction (4) occurs, there can be no ozone destruction at night.

$$BrO + ClO \rightarrow BrCl + O_2 \qquad k_4$$

Reaction one forms Cl and Br directly without the need for photolysis. Reaction (4) does not form Cl and Br directly, so would require something (sunlight, heat, etc) to break the molecule apart in order for the fragments to react with ozone (or BrCl would have to react with O_3 directly)

(f) (2 pts) Knowing that reaction (4) does occur, what does this tell us about the properties of BrCl if ozone depletion does occur in the troposphere?

BrCl probably photolyzes to form Br + Cl, and it must do so in the visible portion of the spectrum in order to occur in the troposphere. As it turns out, BrCl does break down in visible light. (like homework problem 10)

4. (15 pts) The following story appeared on Reuters news on April 27, 2011.

The nation's 25 most smoggy cities improved air quality over the last year, but half the nation's residents still live with unhealthy levels of air pollution, according to an American Lung Association report released on Wednesday. The progress the nation has made cleaning up coal-fired power plants, diesel emissions and other pollution sources has drastically cut dangerous pollution from the air we breathe. The most dramatic improvement has been controlling ozone, commonly known as smog. Still, the report found that 154.5 million people, just over half the nation's population, live in areas where the air is filled with dangerous levels of ozone and particle pollution.

(a) (3 pts) The report gave Boulder County a grade of "F" for ozone, noting that 13 days each year (on average) ozone levels exceeded 75 parts per billion for 8 hours or more. Describe how to convert this mixing ratio of ozone into a concentration, $[O_3]$, in molecules cm^{-3} (you don't need to do the calculation).

$[O_3]$ = mixing ratio x $[O_3]$

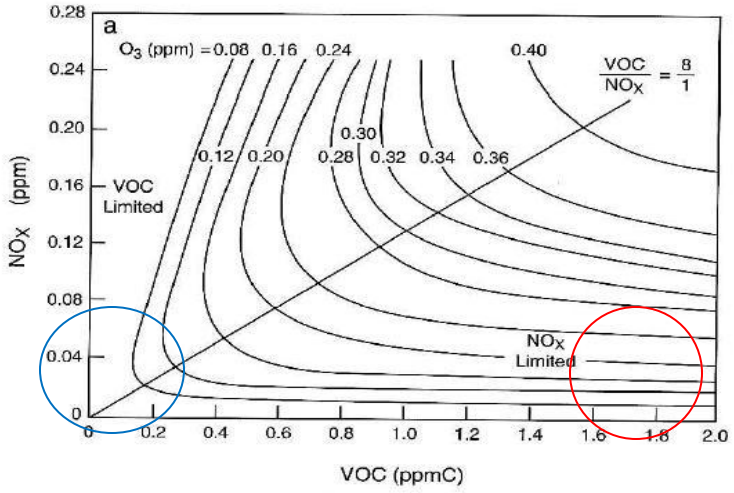
(b) (3 pts) What two quantities (physical characteristics) of the atmosphere would you need in order to do a calculation as required for part (a) using the ideal gas law?

Temperature and pressure (e.g., homework problem 1)

(c) (3 pts) Why do emissions of NO_x ($NO + NO_2$) lead to formation of ozone in polluted regions of the atmosphere?

NO_2 photolyzes in visible light to form O, which is the source of ozone

(d) (3 pts) The State of Colorado requires automobiles to be emissions tested every few years. Using the graph on the next page, explain why a city with high natural abundances of VOCs (e.g., near a forested area) would try to limit vehicular emissions of NOx, whereas a city like Boulder, with negligible (near zero) natural sources of VOCs, would try to limit vehicular emissions of VOCs, in order to reduce formation of ozone and meet EPA attainment standards.



Note for the red circle (high VOC), increasing NOx (vertical direction) will dramatically increase O_3, but a change in VOCs (horizontal direction) will have no impact on ozone (the contour lines are flat…no change with NO_x). For the blue circle, virtually no VOCs, a change in NOx (vertical) has very little impact on ozone (this is because there's nothing for the NOx to react with – in fact, an increase in NOx will actually decrease ozone if NOx > 0.04 ppm). A change in VOCs will have a strong impact on ozone if NOx is non-zero, so this is why regions like Boulder must focus on VOCs (and they should also keep an eye on NOx just to be safe).

(e) (3 points) The straight line in the figure above has a label "VOC/NOx = 8/1", which means that a change in NOx will produce 8 times as much ozone as the same change in VOCs (e.g., a 0.1 ppm change in NOx will produce the same increase in ozone as a 0.8 ppm change in VOC). Using the following reaction scheme for a typical alkane (or hydrocarbon, R stands for H, CH_3, C_2H_5, etc.), explain how this might be the case.

$$R\text{-}CH_3 + OH \rightarrow R\text{-}CH_2 + H_2O$$
$$R\text{-}CH_2 + O_2 + M \rightarrow R\text{-}CH_2O_2 + M$$
$$R\text{-}CH_2O_2 + NO \rightarrow R\text{-}CH_2O + NO_2$$
$$R\text{-}CH_2O + O_2 \rightarrow R\text{-}CHO + HO_2$$
$$HO_2 + NO \rightarrow OH + NO_2$$
$$NO_2 + h\nu \rightarrow NO + O$$

Note that NO is a catalyst – it is consumed, making NO_2 which then produces ozone, but then the NO is recycled. So it doesn't take much NOx to make a lot of ozone. But VOCs are consumed in the reaction, so you need a source to keep generating VOCs in order to keep making ozone. So a small change in NOx can create a large change in ozone relative to a similar change in VOCs.

5. (15 points) The following split photos were taken from the same location at the rim of the Grand Canyon under different conditions. The opposite rim of the canyon is approximately 30 km away. The haze is due to photochemical smog transported from large metropolitan areas to the south and west (Phoenix, Los Angeles, Las Vegas).

(a) (3 pts) A simple relationship between visibility and fine particulate air pollution (or PM2.5) tells us that there was greater than 30 μg m^{-3} of PM2.5 when the photo on the right was taken, whereas it was less than 10 μg m^{-3} for the photo on the left. Based on a 2009 study published in the New England Journal and Medicine (shown in class), would someone's long-term exposure to 30 μg m^{-3} of PM affect their life expectancy, and if so, by approximately how many years?

We noted in class that for each 10 μg m^{-3} increase in particulate matter over background there is a ~0.6 year decrease in life expectancy (in the book they say 1%, so that implies an average life expectancy of 50 years). So this would mean 1.2 for an excess of 20 μg m^{-3}. I gave full credit for 1.8 years, figuring that you understood the concept.

(b) (3 pts) In December of 1952, there was a famous episode of particulate air pollution that resulted in the deaths of 4000 people in one week. In what city did this important event occur, and what two components of the pollution most likely caused the respiratory affects experienced by the residents?

London – smoke and fog. The smoke was soot, and the fog was sulfuric acid (not just water!). A toxic mix.

(c) (3 pts) The 2010 gulf oil spill provided NOAA atmospheric chemists with a rare opportunity to measure aerosol formation from organic molecules. Describe the key new finding about the formation of particulate matter by NOAA scientists.

That it wasn't the most volatile organic compounds that produced aerosols, but, rather, the semi-volatile (the larger carbon chains) that ultimately formed aerosols. This isn't that surprising, really, but it was a great little experiment to prove a hypothesis, which is how science is advanced.

(d) (3 pts) Several important environmental consequences of particles are that they scatter light, thus reducing visibility, and they provide liquid and solid surfaces for heterogeneous chemical reactions. The key property for both of these issues is their surface area density [or SAD = (total particle area)/(volume of air)]. Describe how you would calculate the SAD for an aerosol if you were given the radius of the particles and the total number of particles in a cubic centimeter of air.

Homework #12 – calculate the surface area of a single sphere of radius R using $4\pi R^2$ and multiply by the number of particles in a volume (the number density)

(e) (3 pts) For the submicron ('fine') particles in the right panel of the photo above the SAD was approximately 200 μm^2 cm^{-3}. What additional information would you need to estimate a heterogeneous rate coefficient for hydrolysis reaction of peroxy acetyl nitrate ("PAN") on those particles ("aerosol" means the molecule is in the particle phase)?

$$PAN + H_2O_{aerosol} \rightarrow HNO_{3\ aerosol} + CH_3COOH$$

Basically, homework #13

Rate = $k\,[PAN] = \gamma v A/4\,[PAN]$

v is the velocity of the molecule, in this case PAN, and A is the surface area density (also SAD). Gamma, γ, is the sticking (or reactivity) coefficient – basically the probability of a molecule reacting when it hits the surface of the particle.

6. (13 pts) True or False

___T__ (a) In the troposphere, it typically takes tens of days for air to circle the earth, but it can take 6-months or longer for air to cross the equator.

___F__ (b) Polycyclic aromatic hydrocarbons (or PAHs) are primarily produced by natural processes.

___T__ (c) $CH_3CO.O_2NO_2$ (or PAN = peroxyacetyl nitrate) is important in the atmosphere because it serves as a reservoir of NO_x that can transported long distances from the original source.

___T__ (d) Because molecules like ozone and O_2 absorb solar energy at wavelengths less than 310 nm, molecules that have small cross sections at wavelengths greater than 310 nm have very long photolysis lifetimes in the troposphere.

___F__ (e) The amount of sulfur produced by human activities is insignificant compared to the amount of naturally occurring sulfur.

___T__ (f) Oxidation of VOCs can generate particles, such as those that make up the aerosol "blue hazes" formed over the Smoky Mountains.

___F__ (g) Ozone loss in the arctic boundary layer (i.e., at the surface) is primarily due to bromine that is released from nearby volcanoes.

___T__ (h) A 'termolecular' reaction is one that depends on pressure.

___F__ (i) Absorption of infrared photons causes most molecules to photodissociate.

___F__ (j) In the troposphere, nitrogen oxides are formed mainly by the reaction of N_2O with ozone.

___T__ (k) Fertilization of corn used to produce ethanol as a renewable fuel can actually contribute to global warming by producing N_2O, which is 310 times more efficient at trapping heat than CO_2.

___F__ (m) "Fracking" refers to the process by which sulfur is removed from coal before it burned, in order to avoid having to remove SO_2 emissions with expensive scrubbers.

___F__ (l) Because it costs $50,000 per ton to remove SO_2 from a smokestack, it is impractical to scrub SO_2 from coal-fired power plants.

7. (6 points) The pH of pure water is 7 (meaning that $[H^+] = 10^{-7}$ moles per liter).

(a) (2 pts) What is the typical pH of rain that falls in a rural environment (i.e., far from local sources of pollution, including volcanoes)?

5.6

(b) (2 pts) naturally occurring, long-lived atmospheric constituent increases the acidity of rain in this 'clean' environment and how does it do so?

Carbon dioxide (dissolves in water to form carbonic acid, which is a weak acid, but there's enough CO_2 in the atmosphere to create plenty of H^+ to acidify water.

(c) (2 pts) What human-produced pollutants are most responsible for further increasing the acidity of rain?

SO_2, NOx, organics

8 (a) (4 pts) Pick one student presentation other than your own and summarize the main points.

Any…and you all did really well on this!

(b) (4 pts) What was the most interesting thing you learned in this class? Why?

Another great list…thanks for the compliments and thanks for a great semester!