CHEM173 Final Exam — Spring 2008

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1. Stratospheric Ozone (20 pts: 5, 5, 5, 5)
a) Write the four reactions in the Chapman cycle.
b) What is the typical concentration of ozone in the ozone layer?
c) Is the actual concentration of ozone in the unpolluted ozone layer higher or lower than is predicted by the Chapman cycle alone? Explain what is missing that makes it too high or too low.
d) What three factors are needed to calculate the *rate constants* for the photolysis reactions in part (a)? Which of these factors varies most with altitude? Why?

a) O_2 + hv to 2O, O_3 + hv to O_2 + O, O + O_2 + M to O_3 + M, O_3 + O to $2O_2$
b) 5 to 10 ppmv
c) lower because we have a hole due to CFCs
d) for the reactions in (a), not (b), the factors are absorption cross section, photon flux, and quantum yield. Photon flux varies the most because light is filtered out higher in the atmosphere so less photons are available the lower you are.

2. Ozone Hole (40 pts: 5, 15, 5, 5, 10)
a) Give the layerof the atmosphere and the geographic location of the ozone hole.
b) The following questions refer to the depletion of stratospheric ozone in part (a).
   i) What meteorological feature of the polar regions is needed to transport Cl species downward from above 25km?
   ii) What type of clouds form when stratospheric ice freezes below -80°C?
   iii) What two species release Cl_2 by reactions on stratospheric ice particles?
   iv) What reaction releases Cl from Cl_2 in springtime?
   v) What role do Cl species play when they are in the ozone layer?
c) What is the role of chlorofluorocarbons in the depletion of stratospheric ozone in part (a)?
d) What two catalysts are responsible for approximately (i) 25% and (ii) 75% of ozone loss in the ozone hole? What is the net reaction in each case?

a) It's in the stratosphere over Antarctica
b) Polar vortex, polar stratospheric clouds, HCl and $ClONO_2$, Cl2 + hv to 2Cl, Cl catalytically destroys ozone
c) They provide the chlorine
d) i) Cl, ii) Cl in both sets Cl is the direct sink of O3. ClO is also involved but not used up in either set of reactions and could also be called a catalyst. Net in I) is O+O_3 to $2O_2$, net in ii) is $2O_3$ to $3O_2$

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3. Composition of the Atmosphere (40 pts: 10, 15, 15)

a) Name the five most abundant components of the atmosphere. Give the volumetric percentage of the top two most abundant components.

b) For the following tropospheric constituents, convert from the volumetric percentage to the units specified. In all cases, *show your work*. You should assume 1 atm and 273K, and you may use the approximation that there are 22.4 L/mole air at these conditions. If the exact answer requires long division, please approximate to one significant digit but do make sure that you get the correct order of magnitude.
   i) 0.035% -- convert to [ppmv]
   ii) 0.00001% -- convert to [ppbv]
   iii) $(4x10^{-12})$% -- convert to [molec cm^{-3}]

c) For the following three chemical components of the atmosphere (CO_2, O_3, OH), state which *one* is long-lived (more than 1 year), which *one* is moderately long-lived (1 hr to 1 yr), and which *one* is short-lived (less than 1 hr). State the approximate scale of spatial variability for each of these three classes of atmospheric constituent (global, regional, local).

d) Match the three atmospheric volume percentages listed in part (b) above (0.035%, 0.00001%, $(4x10^{-12})$%) to the most likely of the three chemical constituents in (c) above (CO_2, O_3, OH) to be found in the atmosphere in that concentration or mixing ratio. [Hint: Use each answer only once, and pick the best answer for each using what you know about atmospheric composition, chemical reactions, and chemical lifetimes.]

a) N2 (78%), O2 (21%), Ar, CO2, H2O

b) i) 0.035% = 0.035 X/ 100 air * 1e4/1e4 = 350 X/1e6 air = 350 ppmv
   ii) 0.00001% = 0.00001 X/100 air * 1e7/1e7 = 100 X/1e9 air = 100 ppbv
   iii) [4e-12 molecules X/ 100 molecules air]*[6.022e23 molecules air/mole air]*[1 mole air/22.4 L air]*[1 L air/1000 cm3] = [4e-12*6e23*1*1] /[100*1*22.4*1000] = 24e11/22.4 e6 ~1e5 molec cm-3

c) CO2 is long-lived and globally uniform, ozone is moderate and regionally uniform, OH is short and only uniform over 100's of meters.

d) CO2 is 350 ppm, ozone is 100 ppb and OH is 1e5 molecules cm-3

4. Chemical Families and Cycles (40 pts: 10, 5, 10, 10, 5, 5)
a) What is the largest source of NO_x to the atmosphere? What process(es) is responsible for removing most of the NO_x from the atmosphere?
b) What is the largest source of SO_2 to the atmosphere? What process(es) is responsible for removing most of the SO_2 from the atmosphere?
c) Name the main atmospheric reservoirs of *nitrogen*. For each reservoir, name the chemical compound, write its chemical formula, and identify the oxidation state of nitrogen.
d) Name the main atmospheric reservoirs of *sulfur*. For each reservoir, name the chemical compound, write its chemical formula, and identify the oxidation state of sulfur.

a) fossil fuel burning; wet deposition
b) fossil fuel burning; wet deposition
c) N2 (nitrogen, ox = 0), N2O (nitrous oxide, ox = +1), NO (nitric oxide, ox = +2), NO2 (nitrogen dioxide, ox = +4), NO3 (nitrogen trioxide, ox = +6), HNO3 (nitric acid, ox = +5)
d) H2S (hydrogen sulfide, ox = -2), SO2 (sulfur dioxide ox = +4), CH3SCH3 (dimethyl sulfur, ox = -2), COS (carbonyl sulfur, ox = -2), H2SO4 (sulfuric acid, ox = +6)

5. Smog (40 pts: 5, 5, 10, 10, 10, 10)
a) Define air pollution.
b) What were the main sources and chemical emissions that caused smog in London (in 1952)?
c) What are the main sources and chemical emissions that cause smog in Los Angeles (today)?
d) How is OH related to O_3? Write the two most important reactions.
e) Write the *two limiting steps* for the reaction(s) that control the production rate of ozone in the troposphere (but do not produce ozone themselves). Use these two reactions to write the expression for the production of tropospheric ozone (do not include null cycles).
f) What radical acts as an "atmospheric detergent" in the troposphere? State why it is called a detergent. Name four pollutants that are oxidized by it.

a) air pollution is a condition where compounds are present at levels high enough above ambient concentrations to have a measurable effect on man, animals, or property.
b) SO2 from coal combustion
c) VOCs and NOx from cars or fossil fuel combustion
d) O3 + hv to O2 + O(1D), O(1D) + H2O to 2OH
e) RO2 + NO to NO2 + RO, HO2 + NO to NO2 + OH, P(O3) = k1[RO2][NO] + k2[HO2][NO]
f) OH. It reacts with pollutants and reduces their concentration. CO, VOCs, CH4, SO2

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6. Tropospheric Ozone (40 pts: 10, 5, 25)

a) The following 4 data points describe the 140 ppb ozone isopleth for the urban plume of New York, on the fourth day of ozone-episode simulations [Sillman et al., 1990].

Point	Hydrocarbon emission factor	NOx emissions factor
1	2	0.6
2	1	0.7
3	1	1.5
4	2	2.7

i) What is an ozone isopleth?

ii) Draw the ozone isopleth given by the data above on a graph with axes labeled appropriately.

iii) If the emissions are initially at point 3 (Hydrocarbon=1, NOx=1.5), what will happen to the ozone if NOx emissions are reduced from 1.5 to 1.0? Explain any assumptions you need to make.

b) What is a VOC? What is SOA? State the phase in which each is predominantly found in the atmosphere.

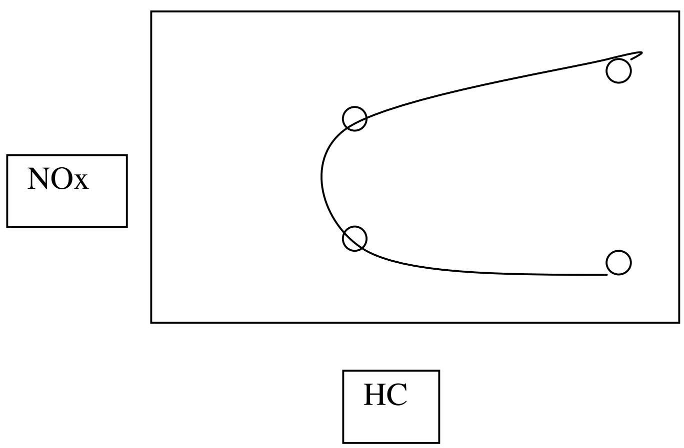
c) CO oxidation in the atmosphere can produce ozone.

i) What is the important atmospheric oxidant in the troposphere that oxidizes CO? What other atmospheric pollutant is needed for CO oxidation to produce more ozone than is lost?

ii) What happens to the ozone production and to the pollutant when the concentrations of the pollutant are very high?

a) i) an ozone isopleth is a line of constant ozone concentration

ii) which goes on which axis?



iii)depends what the isopleths to the right and left of 140 are…

b)volatile organic carbon (gas), secondary organic aerosol (liquid or solid)

c) OH, NOx, when NOx is very high, these two react to form nitric acid and wet deposition occurs

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7. Aerosols and Clouds (50 pts: 10, 10, 5, 5, 5, 5, 10)

a) What is nucleation? Give an example.
b) How does a convective cloud form? Explain the roles of buoyancy and water saturation.
c) Give the name and physical property which *prevents* water from nucleating in the Earth's atmosphere without a large enough preexisting particle.
d) Give the name and physical property which *helps* water nucleate on a particle by providing energy from mixing.
e) For particles composed of the soluble salt shown above, what supersaturation is required in order to activate droplets from particles which are 0.1 μm diameter at 99% RH? Add figure

a) nucleation is the formation of a new phase. Cloud formation.
b) Air rises and cools and the saturation vapor pressure drops so condensation begins.
c) Kelvin, surface tension
d) Raoult, solute or ion
e) ? graph needed

8. Measurement (40 pts: 10, 10, 10, 10)
a) What type of atmospheric chemistry measurements can be made using infrared spectroscopy? Name an example.
b) Why is the detection limit of a technique important for determining if it can be used to measure a chemical component in the atmosphere?
c) If the concentration of submicron particles in the air is 5 $\mu g\ m^{-3}$, what volume of air would you need to pull through a filter to collect 5 g of particle mass for chemical analysis? State any assumptions you use.
d) Name three techniques used to separate gases and particles.

a) chemical composition. ? FTIR?
b) Because concentrations are so low
c) 1e6 m3 assuming all the particles are trapped on the filter and there are no artifacts of additional material or semi-volatiles lost
d) denueder, scrubber, MOUDI (based on centrifugal force)

9. Climate Change (40 pts: 15, 15, 10)

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a) In the next three parts, contrast the 1st (more than 4 Ga ago) and 3rd (up to about 3 Ga ago) stages of the evolution of the Earth's atmosphere.

i) What is the main difference in the chemical nature between the 1st and 3rd stages?

ii) Name two major constituents of the 1st and 3rd stages that illustrate this chemical difference.

iii) What major change led to the development of the composition of the 3rd (most recent) stage?

b) Refer to the diagram below for the following questions.

i) Draw a circle on the diagram around the "albedo" in the diagram below.

ii) What is the name for the specific range of the "longwave" radiation identified below?

iii) Draw a circle around the additional radiation that is radiated back to Earth by the "greenhouse effect"?

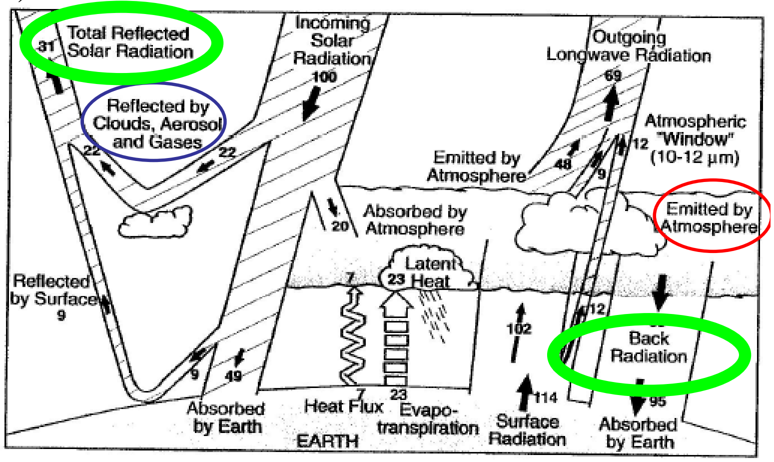

Figure 4.1. The annual mean global energy balance of the Earth-atmosphere system. Numbers are given as percentages of the globally averaged solar energy incident upon the top of the atmosphere (TOA). The 100 units of incoming solar radiation at the TOA represents 342 W m^{-2} (see text).

c) What type of chemical component of the atmosphere has a positive radiative forcing? Give a specific chemical example.

d) Will a positive radiative forcing result in a warming or a cooling of the global mean temperature?

a) first was reducing (CH_4, H_2) , third is oxidizing (O_2, O_3), evolution of plants provided oxygen from CO_2 and water

b) infrared radiation

c) greenhouse gas, CO_2

d) warming

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10. Extra Credit (10 pts)

Name up to ten "Take-Home Messages" that describe atmospheric chemistry on Earth.

1. What atmospheric chemistry is not!!!
2. An ozone hole was unpredictable!!!
3. The Earth's atmosphere is unique!!!
4. OH cleans AND makes pollutants!!!
5. Mix of emissions specify chemistry!!!
6. NO_x increases VOC pollution!!!
7. Particle SIZE matters!!!
8. Clouds are made from particles!!!
9. Most rain is acidic!!!
10. Particle pollution causes cooling!!!