CHEM173 Final Exam **Name**_____

Spring 2007 UCSD ID Number_____

1. Stratospheric Ozone (20 pts: 5, 5, 5, 5)

a) What is the name of the set of reactions that control O_3 formation and destruction in the stratosphere?

b) Write the four reactions named in part (a).

c) What three factors are needed to calculate the *rate constants* for the photolysis reactions in part (b)? Which of these factors varies most with altitude? Why?

d) What is the typical concentration of ozone in the ozone layer?

CHEM173 Final Exam **Name**_____
Spring 2007 UCSD ID Number_____

2. Ozone Hole (40 pts: 5, 15, 5, 5, 10)

a) What is the name for the depletion of the stratospheric ozone layer at the Arctic and Antarctic poles?

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 80C?
   iii) What two species release Cl2 by reactions on stratospheric ice particles?
   iv) What reaction releases Cl from Cl2 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) Write the mechanism responsible for destruction of ozone by NO.

e) State the net reaction for the cycle below. What role does it play in the ozone hole?

$$ClO + ClO + M \xrightarrow{k_1} (ClO)_2 + M$$

$$(ClO)_2 + h\nu \xrightarrow{j_2} Cl + ClOO$$

$$ClOO + M \xrightarrow{k_3} Cl + O_2 + M$$

$$2Cl + 2O_3 \xrightarrow{k_4} 2ClO + 2O_2$$

Write expressions for the rates of destruction of Cl, ClOO, and $(ClO)_2$ in terms of the concentrations of Cl, ClOO, $(ClO)_2$, ClO, O_3, and M and the constants k_1, j_2, k_3, and k_4.

CHEM173 Final Exam **Name**_____
Spring 2007 UCSD ID Number_____

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 units provided to volumetric percentage. 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) CO_2 355 ppmv
   ii) O_3 100 ppbv
   iii) OH 10^6 molec cm^{-3}

c) For the three atmospheric constituents listed in part (b) above, 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). (Each of the three constituents in part (b) above should be used exactly once.) State the approximate scale of spatial variability for each of these three classes of atmospheric constituent.
   j) CO_2 355 ppmv
   ii) O_3 100 ppbv
   iii) OH 10^6 molec cm^{-3}

CHEM173 Final Exam **Name**_____

Spring 2007 UCSD ID Number_____

4. Chemical Families and Cycles (40 pts: 10, 5, 10, 10, 5, 5)

a) What is NO_x? How does NO_x differ from NO_y?

b) What is the most important type of anthropogenic source of NO_x?

c) What is the name for the pathways, interfaces and reservoirs pictured in the diagram below?

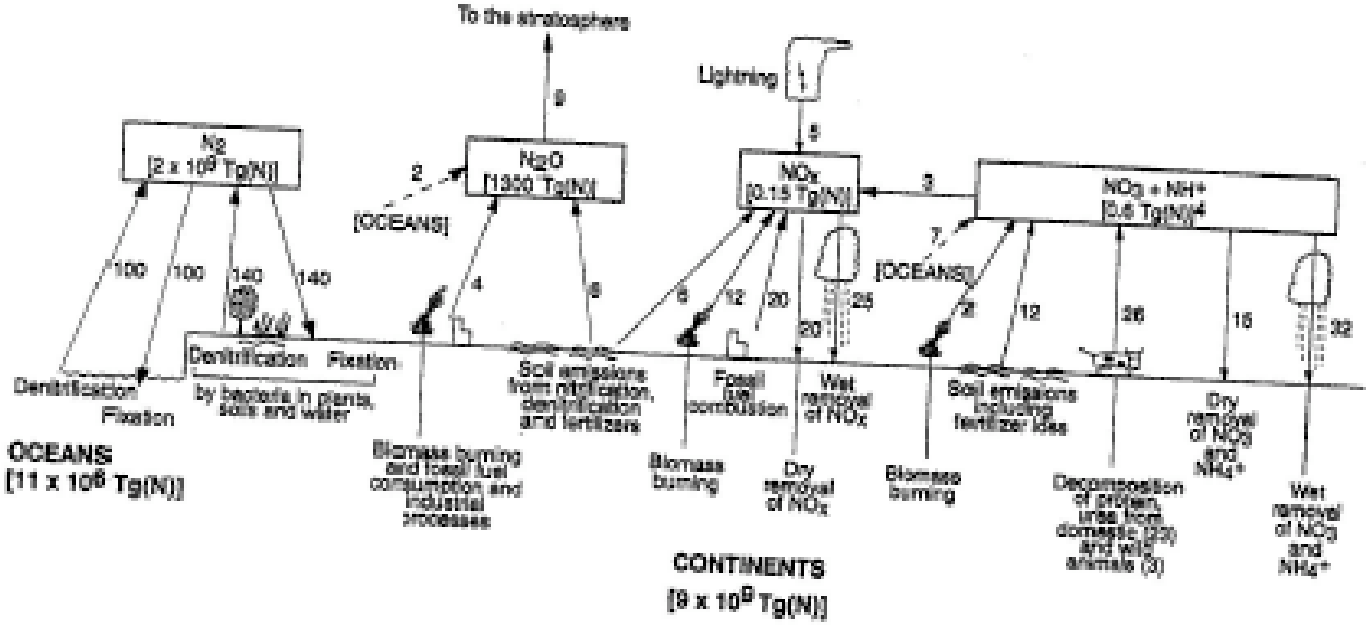


Figure 8.2. As for Fig. 8.1 but for nitrogen-containing gases. Fluxes are in Tg(N) per year.

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.

e) Which reservoir is responsible for the removal of most of the reactive sulfur? What is the process (or processes) responsible for this removal?

f) If the atmosphere contains 0.3 Tg(S) of SO_2 and the total removal rate is 120 Tg(S) per year, what is the residence time of SO_2 in the troposphere?

CHEM173 Final Exam **Name**_____

Spring 2007 UCSD ID Number_____

5. Smog (40 pts: 5, 5, 10, 10, 10, 10)

a) Define air pollution. Give an example of a pollutant and identify what makes it a pollutant in the atmosphere.

b) What happened in the demonstration in class with an orange peel? Which kind of smog has similar chemistry? Which detrimental effect of smog was visible in the demonstration?

c) What is the main chemical component in the smog particles in London (in 1952)? What is the main chemical component in the smog particles in Los Angeles (today)?

d) How is OH related to O_3? Write the most important reactions.

e) Write the *two limiting steps* for the reaction(s) that control the production of ozone in the troposphere. 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.

CHEM173 Final Exam
Spring 2007

Name_____
UCSD ID Number_____

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

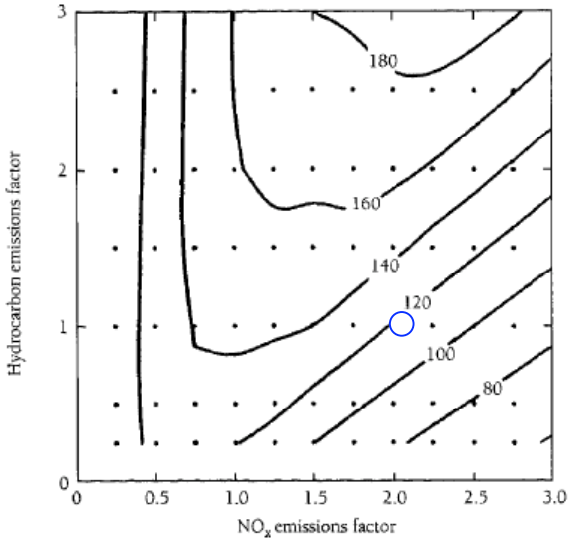


Figure Caption: Peak ozone mixing ratio (in ppb) in the urban plume of New York, on the fourth day of ozone-episode simulations [Sillman et al., 1990].

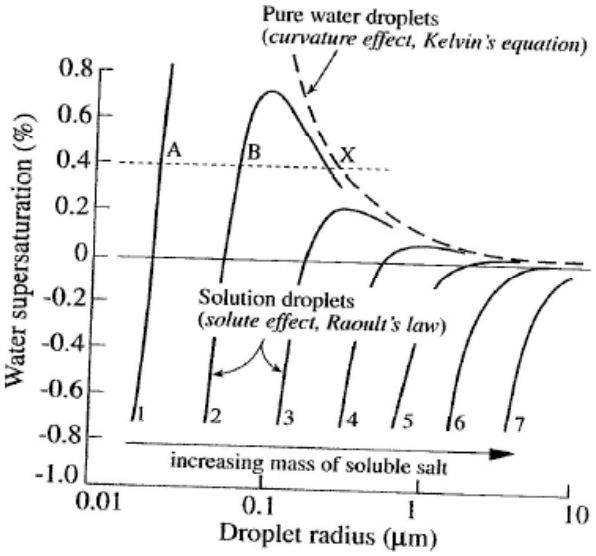
a) Use the figure above for ozone in New York.
   i) What is an ozone isopleth?
   ii) What is the ozone mixing ratio that corresponds to hydrocarbon emission factor of 1 and NO_x emission factor of 2?
   iii) How will the ozone mixing ratio change if the NO_x emission factor increases from 2 to 3?
   iv) At the NO_x emission factor of 2, mark on the plot the hydrocarbon emission factor range for which ozone is sensitive to hydrocarbon emissions.

b) What is a VOC? What is the difference between a hydrocarbon and a VOC? Name a compound that is both a hydrocarbon and a VOC.

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 are the 5 reactions that summarize CO oxidation when the oxidant and the pollutant named in (c-i) are present? Include the role of the pollutant and give the net reaction. Will this set of reactions happen at night? Why or why not?
   iii) What happens to the ozone production and to the pollutant when the concentrations of the pollutant are very high?

CHEM173 Final Exam **Name**_____
Spring 2007 UCSD ID Number_____

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



a) What is saturation? What is supersaturation? Include an equation in terms of the vapor pressure of water and the water saturation vapor pressure.
b) How does the saturation of a warm, moist air parcel change as it rises? Explain what changes to cause this if the total amount of water in the air parcel is constant.
c) What is nucleation? Give an example.
d) What is a Köhler curve?
e) Give the name and physical property which *prevents* water from nucleating in the Earth's atmosphere without a large enough preexisting particle.
f) Give the name and physical property which *helps* water nucleate on a particle by providing energy from mixing.
g) 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?

CHEM173 Final Exam **Name**_____
Spring 2007 UCSD ID Number_____

8. Measurement (40 pts: 10, 10, 10, 10)

a) What type of energy transition is used in infrared spectroscopy? Illustrate with a diagram that shows energy states.

b) What type of energy transition is used in X-ray fluorescence? Does this transition involve singlet or triplet states?

c) Name three techniques for measuring the gas-phase chemical constituents of the atmosphere. For each technique, describe the principle of operation and whether it is an example of spectrometry or spectroscopy.

d) What particle characteristics make it difficult to measure the chemical composition of particles? Include in your answer three characteristics of aerosol particles and describe how each impacts aerosol chemical measurements.

CHEM173 Final Exam **Name**_____
Spring 2007 UCSD ID Number_____

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

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 two major roles played by greenhouse gases.

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

iii) What is the name given to the "total reflected solar radiation" identified on the diagram below?

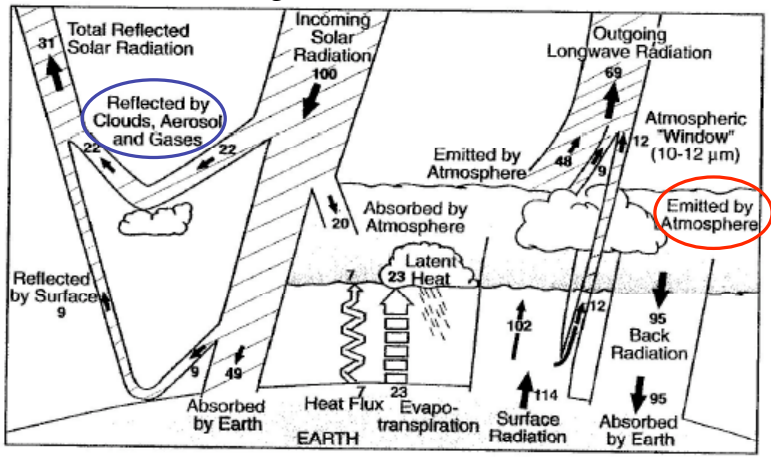


Figure 4.1. The annual mean global energy balance of the Earth-atmosphere system. Numbers are given as percentages of the globally averaged solar energy incident upon the top of the atmosphere (TOA). The 100 units of incoming solar radiation at the TOA represents 342 W m^{-2} (see text).

c) Consider how radiative forcing affects the atmospheric radiation balance?

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

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

Name_____
UCSD ID Number_____

10. Extra Credit (10 pts)
Name up to five "Take-Home Messages" that describe a role that aerosol particles play in atmosheric chemistry.