CHEM173 Review Notes for Midterm 2

Spring 2006

Note that the questions on the midterm are unlikely to be identical to any of the questions that I have given as homework. The idea is instead that the concepts they review will be useful for the exam.

The best way to study for the midterm is to review your notes from lecture, section, and the text. Here is the summary from lecture:

Review for Midterm 2

Chm. Families and Cycles (Ch. 5, 8)	Carbon, Nitrogen, Sulfur	Sources+sinks → reservoirs and residence times
Smog (Ch. 9)	London: SO_x,OH LA: VOC,NO_x,O_3	Pollution+sunlight → health, visibility
Tropospheric Ozone (McElroy 17)	O_3,O*,OH,HO_2, NO_2,NO,HNO_3, CH_4,CH_2O,CO	Ozone levels are *sensitive* to VOCs and NO_x
Particle Composition (Ch. 6.1,2,4)	$SO_4^=$,NO_3^-,NH_4^+, org.C,elem.C, salts,minerals	Chemical make-up varies by SIZE, source, location

The following problems in Hobbs are particularly helpful: Appendix 1 problems 1o-1v, 1x-1z, 1aa-1cc, 18-32, 41-46.

1a (5 pts.). Which free radical is most important in driving nighttime chemistry? Provide the major reaction process(es) that form this species.

1b (5 pts.). Which free radical drives daytime chemistry in urban locations? Provide the major reaction process(es) that form this species.

2. (10 pts.) Draw the temporal profiles (concentration vs. time of day) for the key chemical constituents present during the day that participate in and contribute to photochemical pollution. List the key processes that produce the peak observed for each of the key components.

3. (6 pts.) Provide the key reactions that form nitric acid (HNO_3) during the daytime versus during the nighttime. Denote the physical states of the reactants and products involved in these reactions (i.e. solid, liquid, gas).

5. (5 pts.) Calculate how many naphthalene molecules (MW = 128) are in one 50 nm particle. Show all work to receive credit (density = 1.18 g/cm^3).

6. (6 pts.) What are the major formation routes for ozone in the troposphere and stratosphere, respectively?

8. (4 pts.) Explain the concepts of "good ozone" versus "bad ozone".

9. (4 pts.) Write out the two principal chemical processes than can happen to $O(^1D)$ once it is formed in the troposphere?

10. (6 pts.) Which initial reactions do you expect CH_4 and C_3H_6 to undergo in the presence of hydroxyl radical, respectively? Draw the intermediate products of this initial step in the reaction series. Which molecule do you expect to have a longer atmospheric lifetime in the presence of hydroxyl radical?

11. (8 pts.) Compare and contrast the conditions leading to the formation of London and Los Angeles smog.

14. (6 pts.) List three key factors that determine the relative lifetime of a molecule emitted into the atmosphere.

15. (8 pts.) Draw the Lewis dot structures for O_3 and NO. Include resonance structures where appropriate. Which (if any) of these species are considered free radicals?

16. (6 pts.) Draw a plot showing temperature versus altitude (label axes), showing an inversion layer in the troposphere. What is the term used to describe the change in temperature as a function of altitude?

17. (6 pts.) Rank the amount of vertical mixing that occurs in the planetary boundary layer, free troposphere, and stratosphere from most well mixed to least mixed.

3 (12 points). On a global basis, do anthropogenic or biogenic sources as a whole emit more VOC's? Provide the name and draw the chemical structure of the most highly emitted biogenic VOC (excluding methane). What region of the United States has the highest emissions of this compound?

5 (15 points). Describe the processes responsible for the white cloud forming in the flask during the lecture demonstration.

6a (8 points). List the size range of ultrafine particles and which processes and sources form particles in this size mode. 0.001 μm – 0.1 μm

6b (8 points). List the size range of accumulation mode particles and which processes and sources form particles in this size mode.

6c (8 points). List the size range of coarse mode particles and which processes and sources form particles in this size mode. 1um – 10Xum mechanical generation

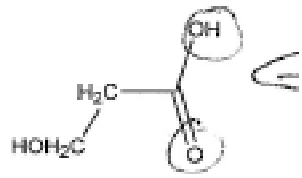
7 (10 points). Draw a curve relating the atmospheric lifetime of particles (as I showed in lecture) to their size (lifetime (y-axis) vs. particle size (x-axis)). Explain the loss processes responsible for the shape of this curve.

8b) Does the presence of water increase or decrease the amount of scattering by a particle? Why?

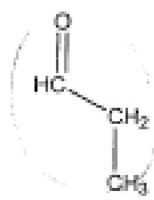
8i) List the key property of a molecule that determines whether the species will be present in the particle versus gas phase.

8j) Which of the following molecules would you expect to be more in the particle phase than the gas phase (a) or (b)?

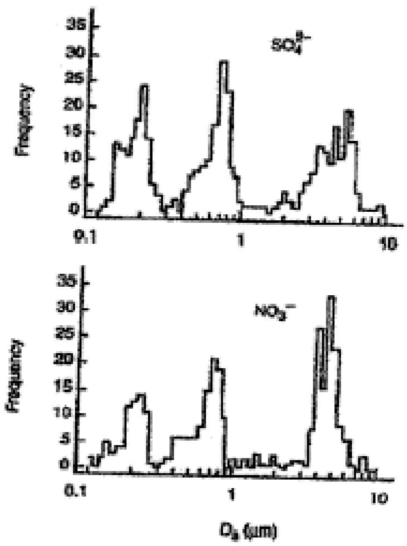
a)



b)



9 (20 points). In the spaces provided below, write out the chemical reactions which produce sulfate and nitrate in the 3 modes observed between 0.1 and 10 μm shown in Figure 9.37 shown below. Be sure and indicate the physical states of all reactants and products.



9a) Smallest mode sulfate and nitrate.

9b) Medium mode sulfate and nitrate.

9c) Largest mode sulfate and nitrate.

9d) Describe the key difference/s in the composition of particles in the small vs. middle mode

9. Draw the typical size distribution (mass distribution; $\mu g/m^3$) for an atmospheric aerosol in a polluted environment and provide the names for the different modes.

7. Are gases or particles more effective at scattering light in the atmosphere? Which tropospheric gas is the most significant absorber of light?

6. Which properties determine how effective a particle is at scattering or absorbing sunlight?

(13) List 3 sources of PM2.5.

(14) Describe how the composition varies as a function of size for particles in the troposphere.

2. Draw the Lewis dot structures for O_3, NO, and NO_2. Are they free radicals?

3. In an indoor atmosphere, for NO_2 the value of the first order rate constant has been estimated to be 1.28 h^{-1}. Calculate its residence time.

11.) What is the most abundant hydrocarbon species in the atmosphere? What is its approximate concentration and how much is it increasing per year (in %)?

10. Provide one common anthropogenic and one common biogenic source for NOx in the troposphere.

7.) In #/cm^3, approximately how many hydroxyl radicals exist in the troposphere under polluted daytime conditions.

5.) What are the major formation routes for ozone in the troposphere and stratosphere, respectively?

I-1 Is the following statement true or false? Clearly explain your answer. "Ozone mixing ratios peak in the afternoon even though mixing depths are usually maximum in the afternoon".

I-3 What are tropospheric chemical cycles? Name the reservoirs of chemical species in the Earth system.

II-1 Mention **five** biological and **two** geochemical sources of gases in the troposphere and provide examples of the main gases released from those sources.

II-2 What are the main sources of OH in the urban troposphere?

II-3 What are the main differences between London-type smog and Los-Angeles type smog?

III-1 Write down **ALL** the steps involved in the oxidation of acetaldehyde in the troposphere together with those responsible for ozone formation. How many molecules of ozone and OH can potentially be formed for each acetaldehyde molecule that is oxidized? Assume that acetaldehyde and formaldehyde molecules photodecompose after absorption of UV light from sunlight.

2) The tropospheric concentration of OH radicals ___________ at night.
(a) drops quickly (b) does not drop (c) increases quickly (d) increases slowly

3) (See Figure at the end of the Midterm) If VOCs mixing ratios are 1.5 ppmC and ozone mixing ratios are 0.16 ppmv the best regulatory method of reducing ozone (if only the effects of NOx (g) and VOCs on ozone are considered) is to ___________________.
(a) reduce NOx emissions (b) increase NOx emissions (c) reduce VOCs emissions (d) increase VOCs emissions

4) (See Figure at the end of the Midterm) The residence time of methane with respect to its efflux can be calculated to be ________.
(a) 9.5 yrs. (b) 9.7 yrs (c) 10.3 yrs (d) 159 yrs

5) Knowing that the final concentration of a chemical involved in a first-order reaction (with a lifetime of 2 min) was $5*10^{10}$ molecules/ cm^3 and that the reaction took place for 10 minutes, it is possible to calculate that the original concentration of the chemical compound was ___________. (p= 1 atm. T=25^oC)
(a) 276 ppbv (b) 301 ppbv (c)15 pptv (d)13 pptv

III-2 Using the key reactions involved in HOx chemistry as listed in **Table 17-1** (and their corresponding rate constant values) calculate the chain length for the HOx cycle at the equatorial surface for the tropospheric conditions listed below. Also, derive an expression for the steady state concentration of OH radicals. Assume steady state conditions for $O(^1D)$ and a total density of air molecules of $3*10^{\wedge 19}$ cm^{-3}.

Tropospheric Conditions

Species	**Mixing Ratio**
H_2O	0.015
H_2O_2	30 ppt
O_3	60 ppb
NO	20 ppt
CO	$1*10^{-7}$
CH_4	$1.7*10^{-6}$
NO_2	40 ppt
OOH	40 ppt