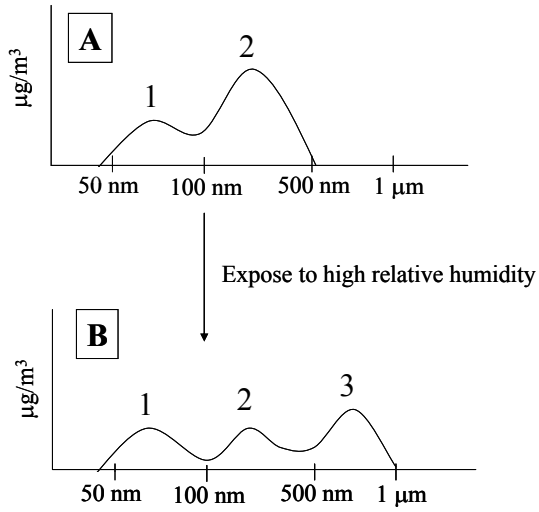
Name:_____KEY_____

Chemistry 173
Midterm #2
Spring 2004

Total Points: /125

1. Two hypothetical atmospheric particle mass distributions are shown below. "A" transforms into "B" upon being exposed to high relative humidity (water vapor). Discuss the processes that lead to this shift at high relative humidity (i.e. extra water). Specifically, detail the composition differences between Modes 2 and 3 that lead to this shift. Note the size range of interest is 0.1-1 μm (Modes 2 and 3 are accumulation mode particles). (12 points)

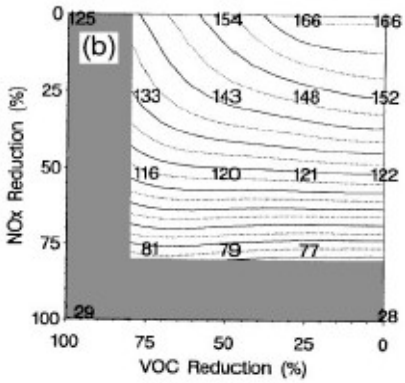


Upon exposure to water, mode 2 splits into two particle size modes (2 and 3). The reason only certain particles grow is because these are composed of hydrophilic species (oxidized organic species and ions such as ammonium, nitrate, sulfate). Thus, mode 2 is composed of EC and hydrophobic OC species (i.e. long chain hydrocarbons). Mode 3 particles are composed of EC (possibly), hydrophilic OC species (i.e. acids, oxidized organic species), water soluble ions (i.e. ammonium, sulfate, nitrate), and water they absorbed upon exposure to high RH.

2. Provide the name of the most highly emitted biogenic (NMHC) VOC. Approximately, what fraction of the total global biogenic VOC's does it represent? (8 points)

Isoprene, roughly 50%

3. Use the ozone isopleth below to explain whether this city is in a VOC- or NOx-limited regime (points are based on your reasoning—guesses will be worth zero points). Given this information, what is the best strategy to reduce the production of ozone? (10 points)



NOx limited. Increasing the reduction of NOx reduces the amount of ozone as shown on the isopleth. Reducing VOC emissions does not have much impact on ozone concentrations however. This city should increase its regulation of NOx emissions. Cars are a major source of NOx. Increase use of catalytic converters is one possible strategy to reduce NOx emissions.

4. Write out two chemical processes that are most responsible for the formation of sub-micron nitrate versus super-micron nitrate (Hint: there are different counter (positive) ions for each). (10 points)

$NH_3(g) + HNO_3(g) \leftrightarrow NH_4NO_3(s)$ (sub-micron mostly)

$NaCl(s) + HNO_3(g) \rightarrow NaNO_3(s) + HCl(g)$ (super-micron mostly)

5. List the parameters that are required to calculate the photolysis rate of a molecule? Which of these parameters is/are wavelength dependent? (9 points)

p. 76 in book: Eqn. OO

Radiation, absorption, and quantum yield for photolysis
All 3 of these are wavelength dependent

6. Write out the 4 major terms which make up b_{ext}. What is the largest term typically in a polluted environment? What is the relationship between b_{ext} and visibility? (12 points)

$b_{ext} = b_{ag} + b_{sg} + b_{sp} + b_{ap}$
a = absorption, s = scattering, p = particles, g = gas
b_{sp} is largest
b_{ext} is inversely proportional to visibility

7. Explain the meaning of the terms external and internal mixture. Name one analytical method that gives you information for each case (i.e. total of two). (12 points)

Internal mixture assumes all particles of same size have identical composition. (bulk filter collection)

External mixture assumes individual particles of the same size can have different composition. (ATOFMS or electron microscopy)

8. In the figure below, an FTIR spectrum is shown of particles collected from the Smoky Mountains, Tennessee. Explain the type of sampler used to collect this sample (hint: the composition of a specific size range is shown). This sample was first rinsed with hexane and no change was observed. Explain what the acetone and water rinses tell you about the composition of the sample (i.e. which species are removed with acetone versus water?). Do any of these rinses tell you about the age of the sample and if so which one(s) and why? (14 points)

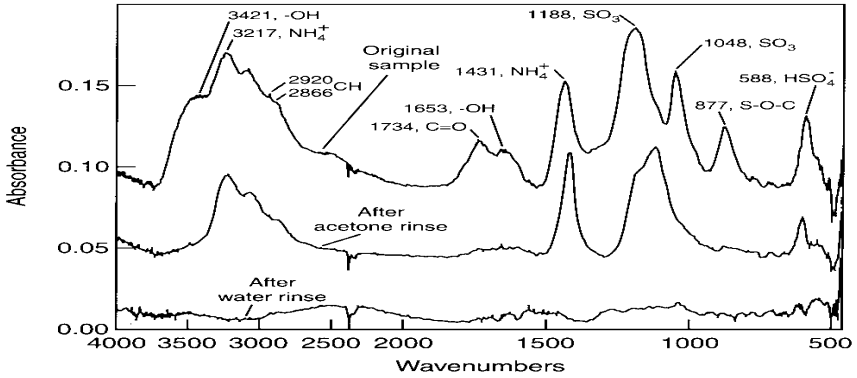


FIGURE 9.50 FTIR spectra of particles from the Smoky Mountains, Tennessee, with diameters between 0.5 and 1.0 μm (top spectrum), after rinsing with acetone (middle spectrum) and then with water (bottom spectrum) (adapted from Blando *et al.*, 1998).

Initially, sample washed with hexane. No change—so very few non-polar organic compounds (like dissolves like)

Then, sample washed with acetone—oxidized (polar) organics removed by wash.

Final wash with water—removes water soluble ions

All rinses tell you something about age. Hexane says no "fresh" (non-reacted organics), acetone says there were oxidized organics (formed by reactions in the atmosphere), and water tells you these particles had built up ammonium and sulfate (secondary species formed from gas phase ammonia and sulfuric acid reactions).

9a. Define the gas-particle partitioning coefficient (K_p) in words as well as in the form of a mathematical expression as shown in lecture (and your book). (8 points)

Most important fact: Kp is a constant!!

$K_p = (F/TSP)/A$

K_p quantifies the relative partitioning of a particular species between the gas and particle phases. It is a CONSTANT for a given temperature and a given species.

9b. If species A has a smaller K_p than species B, in relative terms, would you expect more of A to be in the gas or particle phase than B? (4 points)

A larger fraction of A will be in the gas (over particle phase) than B.

9c. Use the equation in 11a to explain how the absolute mass concentration of all particles in the atmosphere changes the relative partitioning of semivolatile species to the particle phase versus the gas phase (i.e. if you have more particulate pollution, do you expect more or less semivolatile species to exist in the particle phase and why)? (6 points)

If you have more particulate pollution, this means TSP increases.

$A + TSP \leftrightarrow F$

If TSP goes up, the above equilibrium (A is gas and F is particle phase) will shift to the right (based on LeChatlier's principle). Looking at equation in 11a, if TSP goes up, A must go down and F must go up for Kp to be constant. This means more semivolatile species will exist in particle phase.

10. Which of the 3 molecules (propane, butane, iso-butane) would you expect to react with OH the fastest and why? Show where OH will react with the molecule and write the mechanism for the reaction up to the formation of the alkoxy radical ($RO^{\cdot}$) in the polluted troposphere. (8 points)

Isobutane. Bigger and also branched (so forms most stable radical intermediate).

See notes.

11. 500 nm particles can exist in the atmosphere for approximately what timescale? As particles age, do you expect them to become more hydrophobic or hydrophilic and why? Do you expect more species to exist in the particle phase or gas phase as gases age and why? (12 points)

Days to weeks. They will become more hydrophilic via oxidation reactions (which lead to more polar compounds which are more water soluble due to increased H-bonding). As gases age, they become more oxidized—this increases their boiling point and lowers their vapor pressure and leads to more in the particle phase.