CHEM173 Midterm 2

Spring 2007

Name________________________

UCSD ID Number_____________________

1. Chemical Families and Cycles (60 pts: 10, 10, 10, 10, 10, 10)
a) What is NO_x? What is the name for the chemical family that includes precursors and products that can be easily converted to or from NO_x?
b) 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.
c) What is the Sulfur cycle? Describe its components, interfaces, and processes.
d) What is the most important type of anthropogenic source of SO_x?
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?

a) NO_x is the chemical family consisting of nitrogen oxides NO, NO_2 and NO_3. Mostly NO and NO_2 is okay too. NO_y is the chemical family that includes precursors and products that can be easily converted to or from NO_x, such as PAN, HONO.

b) The four atmospheric reservoirs of nitrogen are nitrogen N_2 (0), nitric oxide NO (+2) plus nitrogen dioxide NO_2 (+4) plus nitrogen trioxide NO_3 (+6), nitrate NO_3^- (+5) plus ammonia NH_4^+ (-3), and nitrous oxide N_2O (+1).

c) The Sulfur cycle is the pathways by which and reservoirs through which compounds of nitrogen are transferred among the atmosphere, the hydrosphere (including the oceans), the biosphere (including plants), the cryosphere, and the geosphere (including soil). The primary interfaces across which sulfur is transferred are the ocean-atmosphere and the biosphere-atmosphere interfaces. The processes that control these transfers include combustion emissions (fossil fuel and biomass, anthropogenic and natural) of SO_2, volcanic emissions of SO_4^{2-} and SO_2, soil emissions of H_2S and COS, and algae production of DMS and CS_2, and wet/dry deposition of SO_4^{2-} and SO_2 to the ocean and land surfaces, as well as in situ transformations.

d) Fossil fuel burning.

e) Most of the reactive sulfur is removed by wet deposition or precipitation as SO_4^{2-}.

f) τ_{SO2}=M/F=0.3/120=0.0025 a or 22 hr.

2. Smog (60 pts: 10, 10, 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 reaction(s) that control the production of ozone in the troposphere.
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 any atmospheric condition in which substances are present at concentrations high enough above their normal ambient levels to produce a measurable effect on man, animals, vegetation, or materials.

b) The orange demonstration used high O_3 to cause VOC oxidation of the terpenes from the orange; the products of the VOC oxidation have low volatility so they condense and grow particles large enough to visibly scatter light. The orange demonstration is very similar to photochemical smog, in which high O_3 results in VOC oxidation, the products of which condense and grow particles large enough to visibly scatter light. Smog is a severe pollution episode, usually characterized by severe detrimental effects on visibility, health, and crops. In the orange demonstration, light scattering by particles illustrated the effect of reduced visibility.

c) London fog results from SO_2 emitted by combustion of coal which is oxidized on particles to form sulfate. Los Angeles photochemical smog involves gas phase reactions with NO_x and VOCs to produce high O_3, and high amounts of organics (SOA) and nitrates in particles.

d) $O_3 + h\nu \rightarrow O_2 + O(^1D)$ (or O^*)

$O(^1D) + H_2O \rightarrow 2OH$

$O(^3P) + O_2 \rightarrow O_3$

e) $HO_2 + NO \rightarrow NO_2 + OH$

$RO_2 + NO \rightarrow NO_2 + RO$

f) The hydroxyl radical OH is the "atmospheric detergent" because it causes gas-phase oxidation of pollutants: e.g.

$SO_2 + OH \rightarrow \ldots \rightarrow H_2SO_4 + \ldots$

$NO_2 + OH \rightarrow \ldots \rightarrow HNO_3 + \ldots$

$CH_4 + OH \rightarrow \ldots \rightarrow CO + \ldots \rightarrow CO_2 + \ldots$

$NH_3 + OH \rightarrow \ldots \rightarrow NO + \ldots$

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3. Tropospheric Ozone (80 pts: 40, 10, 30)

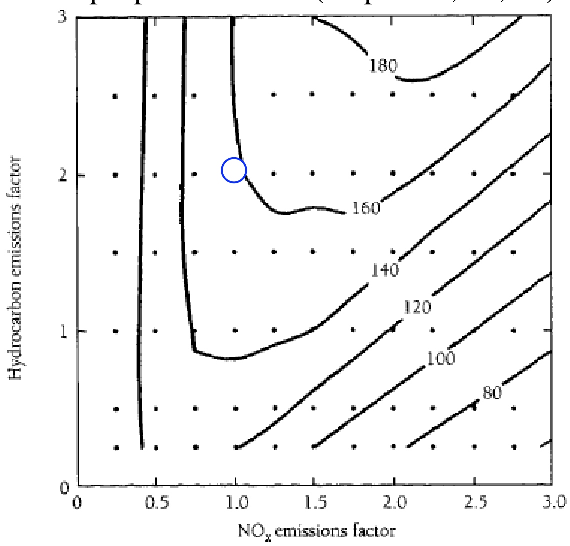

Figure Caption: Peak ozone mixing ratio (in ppb) in the urban plume of New York, on the fourth day of ozone-episode simulations [Sillman et al., 1990].

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 2 and NO_x emission factor of 1?
   iii) How will the ozone mixing ratio change if the NO_x emission factor increases from 1 to 3?
   iv) At the NO_x emission factor of 1, 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?

a-i) An ozone isopleth is a line showing constant ozone concentration.

a-ii) 165 ppb.

a-iii) It will decrease by 30 ppb to 130 ppb.

a-iv) From hydrocarbon emission factor of 0 to 1.5 at NO_x emission factor of 1.

b) VOC refers to volatile organic compounds. Hydrocarbons include molecules containing H and C, but some long-chained alkanes are not volatile, so they are not VOCs; VOCs can include O, S, and other atoms so not all are hydrocarbons. A compound that is both a VOC and a hydrocarbon is α-pinene (also CH_4, ethane, benzene).

c-i) OH; NO_x; no, sunlight is also needed.

c-ii) $CO+OH \rightarrow CO_2+H$; $H+O_2+M \rightarrow HO_2$; $HO_2+NO \rightarrow NO_2+OH$; $NO_2+hv \rightarrow NO+O$; $O+O_2+M \rightarrow O_3$;; Net $CO+2O_2+hv \rightarrow CO_2+O_3$.

c-iii) At very high NO_x, HNO_3 is produced and removed by wet and dry deposition, and the rate of O_3 production begins to decrease.

4. Particle Composition (50 pts: 10, 10, 20, 10)
a) What is an aerosol? Identify all required constituents and their physical states.
b) What are the main chemical components of atmospheric aerosol particles? For each component, specify their primary source(s) and approximate size.
c) What is the accumulation mode? How big are particles in the accumulation mode? What is the composition of these particles in the troposphere?
d) What is the approximate size of particles that have the most detrimental effects on (i) visibility? (ii) health? For each answer, state why the size makes those particles effective.

a) An aerosol is a colloidal suspension of liquid or solid particles in a gas.
b) The main chemical components of atmospheric aerosol particles are sulfates (combustion, 0.1 to 1 μm), nitrates (combustion, 0.1 to 1 μm), ammonium (0.1 to 1 μm), organic carbon (combustion, 0.01 to 1 μm), elemental carbon (combustion, 0.1 to 1 μm), sea salts (ocean wave-breaking, 1 to 10 μm), minerals (urban and desert dust, 2 to 20 μm).
c) The accumulation mode is the peak in particle number distribution that forms from the growth and coagulation of smaller particles. Particles in the accumulation mode have diameters between 0.1 to 1 μm. Accumulation mode particles consist of sulfates and organics, with some unidentified components (and some nitrates, trace metals and salts).
d-i) Particles with the most effects on visibility have diameters ~1 μm, because those sizes are most efficient at scattering light.
d-ii) Particles with the most effects on health have diameters smaller than 1 μm (or 2.5 μm), because those sizes are most efficient at depositing in lung tissue rather than being filtered or exhaled.