**10.571 Atmospheric Chemistry and Physics**

**Homework Problem Set Number 1**

**Assigned 28 February 2006**
**Due Date7 March 2006 (No later than 5:00 pm)**

**Problem 1.1 – The Kyoto Protocol and its Relevance to Urban Air Pollution**

In class we have been discussing air pollution problems that range in scales from local to global. At present much of the discussion in newspapers, radio and TV is about global climate and in particular about the impact of carbon dioxide ($CO_2$). Prepare a <u>one</u> page summary of the Kyoto Protocol, be sure to address its organizational form, who are the signatories, what emission control options are being proposed etc. Once you understand the protocol discuss its relevance to solving urban scale photochemical air pollution problems. Please include the appropriate citations to web sites, papers, books that you use to prepare you memorandum.

**Problem 1.2 – Combustion Chemistry and Air Quality Standards**

The balanced chemical equation for the complete combustion of a general hydrocarbon fuel $C_xH_y$ is given by

$$C_xH_y + \left( x + \frac{y}{4} \right)O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O$$
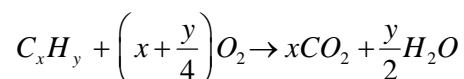
(a) If 1.0 mole of $C_xH_y$ is completely burned, show that 3.7[x + (y/4)] moles of (unreacting) nitrogen will be contained in the emissions.  Hence, write an expression, in terms of $x$ and $y$, for the total number of moles of gases in the emissions.

(b) In reality, combustion in cars converts all of the hydrogen in the fuel to $H_2O$ and all of the carbon in the fuel to varying amounts of $CO_2$ and CO depending on the availability of oxygen. If a fraction $f$ of the $C_xH_y$ is provided in excess of that required for complete combustion, derive an expression in terms of $f$, $x$, and $y$ for the mole fraction of CO in the emissions (i.e., the ratio of the number of moles iof CO to the total number of moles in the emissions).  Assume that oxygen is made available to the fuel at the rate required for complete combustion (even though complete combustion is not achieved), and that the only effect of the excess $C_xH_y$ is to add CO to the emissions and to change the amount of $CO_2$ emitted.

(c) Assuming that $CH_2$ is a reasonable approximation for a general hydrocarbon fuel, use the result from (b) to determine the concentrations (in ppmv and percent) of CO in the emissions from an engine for the following values of $f$:  0.0010, 0.010, and 0.10. Compare these numbers to the US National Ambient Air Quality Standards (NAAQS) for carbon monoxide.

**Problem 1.3 – Wavelength ranges for photolysis**

Nitrogen dioxide ($NO_2$) and formaldehyde (HCHO) are important species that participate in the photochemistry occurring in the troposphere. Look up the bond

dissociation energies for N-O, N=O, H-C, C=O,… and then calculate the longest wavelength of incoming solar radiation that is likely to cause the molecules to dissociate. Compare these wavelength against the quantum yields published in the NASA Kinetics report "Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies Evaluation Number 14 – what do you conclude? (Report URL is http://jpldataeval.jpl.nasa.gov/pdf/JPL_02-25_rev02.pdf)

## Problem 1.4 – Photolysis Rate Constants for Formaldehyde

Formaldehyde is an important photochemically active species in the troposphere. There are two possible photolysis pathways:

$$CH_2O + hv \xrightarrow{\quad 1 \quad} HCO + H$$
$$\xrightarrow{\quad 2 \quad} CO + H_2$$
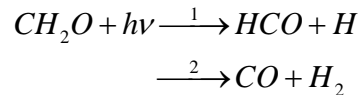
The reaction rate constant for each of these steps is of the form

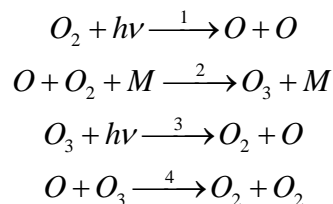$$k_j = \int_0^\infty \sigma_j(\lambda)\Phi_j(\lambda)I(\lambda)d\lambda$$

where $\sigma_j$ is the absorption cross section, $\phi_j$ is the quantum yield and $I$ the actinic flux. Using the wavelength dependent actinic flux data shown in Table 3.4 of Seinfeld and Pandis (p. 146) and the absorption cross section/quantum yield data from Table 4.19 in the NASA Kinetics report "Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies Evaluation Number 14 determine the photolysis rate constants for each of these reactions at latitude 40° North at noon on January 1 and July 1. What then are the characteristic time scales for these reactions? (The NASA report can be found at the following web site - jpldataeval.jpl.nasa.gov/pdf/JPL_02-25_rev02.pdf. How do these numbers compare to the values shown in Table 5.4 p.297 of Seinfeld and Pandis?

## Problem 1.5 – Estimation of concentration

If you take a deep breath what is the likelihood that a nitrogen molecule now in your lungs was also at one time also in the lungs of Albert Einstein?

## Problem 1.6 – Catalytic Cycles

One of the earliest puzzles of atmospheric chemistry was to explain the presence of ozone in the stratosphere. In 1930 Chapman proposed a simple, four step, chemical scheme

$$O_2 + hv \xrightarrow{\quad 1 \quad} O + O$$
$$O + O_2 + M \xrightarrow{\quad 2 \quad} O_3 + M$$
$$O_3 + hv \xrightarrow{\quad 3 \quad} O_2 + O$$
$$O + O_3 \xrightarrow{\quad 4 \quad} O_2 + O_2$$

(a) Derive the differential equations for the concentration dynamics of each species.

(b) Show that $[O] + 2[O_2] + 3[O_3]$ is constant, why should this result be obvious?

(c) Assuming photochemical equilibrium derive an expression for the rate of change of the concentration of [$O_3$] in terms of the concentrations of atomic oxygen [$O_2$] and the third body [M].

(d) Using the results from part (c) look at the vertical profile of [$O_3$] in Figure 4.6 of Seinfeld and Pandis and explain the shape of the vertical ozone distribution.

(e) While the Chapman mechanism explains the basic characteristics of the observed [$O_3$] profile its predictions are too high by about a factor of 2. There must be other loss processes. Typically losses arise from catalytic cycles of the form

$$X + O_3 \longrightarrow XO + O_2$$
$$XO + O \longrightarrow X + O_2$$
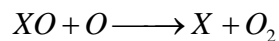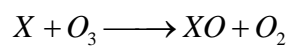
where X is a free radical catalyst (H, OH, NO, Cl, or Br). Explain how these species could catalyze the ozone destruction.