**10.571/12.806 Atmospheric Chemistry and Physics**

**Final Exam**

**Assigned 9th May 2006**

**Due Date 18th May 2006 (No later than 5:00 pm)**

**Instructions**

1. The exam is open book, open notes. There are 3 pages in this exam.

2. You can use notes, problem sets and computer programs used in the course

3. The only people you can ask for help or clarification are the instructors Gregory McRae, Ron Prinn, or the teaching assistant.

4. You have 16 working hours to complete the exam. Please write how long you took (you can take less than the allotted time!) on your exam solution.

5. There are 2 Questions on the exam, each of equal weight. Please make sure that you clearly describe your reasoning and identify the answer. If you cannot complete a question at least lay out a path for how you might solve the problem.

**Problem Number 1 – Atmospheric Chemistry of Ethanol (100 points)**

Considerable research effort in the United States, Europe, and Japan is being directed towards developing an ''ethanol economy'' in which ethanol would be expected to replace a large fraction of oil that is currently used for transportation fuel. At present ethanol in the US is mostly made from corn and in Brazil from sugar cane. In the US typically only the corn kernels are used for ethanol production but there are opportunities to improve the fuel yield by processing the primary cellulosic components like the stalks and leaves.

Many claims about the advantages of the ethanol economy have been published which argue or assume that ethanol will be a widely available, clean, safe fuel. Before widespread use of ethanol is adopted it is critical to understand its atmospheric chemistry and identify if there are likely to be any adverse impacts.

**Part 1 – Combustion Stoichiometry of Ethanol ($C_2H_5OH$) (20 points)**

One of the frequently cited advantages of ethanol is that because it contains oxygen it can assist in the combustion processes that occur at high altitude. Compare the combustion stoichiometry for pure ethanol at sea level with those that might occur in a car in Denver (The Mile High City)

**Part 2 – Reaction Mechanism for Ethanol Photoxidation (30 points)**

Using class notes, Seinfeld and Pandis develop a detailed reaction mechanism and associated reaction rate constants for ethanol photo-oxidation in an urban atmosphere. Comment on the maximum number of NO to $NO_2$ conversions.

**Part 3 – Atmospheric Lifetimes (20 points)**

Using typical values for photolysis rates and OH concentrations estimate the atmospheric lifetime of ethanol.

**Part 4 – PAN Production (30 points)**

Peroxyacylnitrate (PAN - $CH_3C(O)O_2NO_2$) can be formed from the photoxidation products of ethanol. One of the reasons for the interest in PAN is that it is a very potent phyto-toxicant (i.e. it can cause crop and forest damage) as well as a down wind source of $NO_x$. Using typical day-to-night temperature variations explore the equilibrium

$$CH_3C(O)O_2 + NO_2 + M \Leftrightarrow CH_3C(O)O_2NO_2 + M$$

and explain why PAN can be a source of $NO_x$ downwind from a city.

**Advisory note:**
A solution to this problem will require that you make a lot of assumptions, please make sure that you thoroughly explain your reasoning. For example, in some cases you may need to make estimates of reaction rate constants.

**Problem Number 2 – Atmospheric Residence time and Inverse Methods (100 Points)**

Consider a simple idealized global atmospheric model consisting of two boxes with equal total air mass; one box for the northern and the other for the southern hemisphere. Assume that interhemispheric transport for a particular trace gas is proportional to the difference $(M_n – M_s)$ between the masses of that gas in each hemisphere divided by an exchange time $t_{ex}$ of 1 year. Also assume that the atmospheric chemical lifetimes are $t_n$ and $t_s$, and the surface emissions are $E_n$ and $E_s$ for each hemisphere. Write down the two time-dependent continuity equations which express the rate of change of the trace gas masses ($M_n$ and $M_s$) in each hemisphere. Then assume a steady-state and derive analytical expressions for $M_n$ and $M_s$. Using these steady-state $M_n$ and $M_s$ as initial values, integrate the two time-dependent continuity equations with one-month time steps for 5 years for the imaginary trace gas mythane assuming the following: $E_n = 500$ Tg/year, $E_s = 100$ Tg/year, $t_n = 9.0/(1 + f_n)$ years and $t_s = 8.5/(1 + f_s)$ years, where $f_n(t)$ and $f_s(t)$ are sinusoidal functions with 12-month periods peaking at the time of maximum OH concentrations in each hemisphere and with amplitudes of 0.1. Comment on the independence of the solutions from their initial values after 1, 2 and 4 years. Now, using two further runs, compute the partial derivatives of $M_s$ and $M_n$ with respect to $E_s$ and $E_n$ to form the 2 x 2 Jacobian matrix H for use in a Kalman filter. Then, considering the $M_n$ and $M_s$ time series in the first run for years 3-5 as "observations," use the Kalman filter to solve for $E_n$ and $E_s$. For this purpose assume that each "observation" has a 1 sigma uncertainty of 1%, the transition matrix M is the identity matrix, and the initial guesses for $E_n$ and $E_s$ are $480 \pm 480$ and $120 \pm 120$ Tg/year (1 sigma errors) respectively. Repeat this first inversion but now using "observational" uncertainties of 10% and initial guesses of $300 \pm 300$ Tg/year for both $E_n$ and $E_s$. Finally, repeat this second inversion using a system random forcing covariance matrix $Q = 0.1P$ where P is the estimation error covariance matrix. Compare the estimates of $E_n$ and $E_s$ from each of these inversions to their true values of 500 and 100 Tg/year. Using the intuitive concepts discussed in the class, provide reasons for any differences.