**AOSC 434**

**Homework Set 3**

**Kinetics and Atmospheric Lifetimes**

**Due: March 13, 2018**

**12 points possible**

NAME\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

1. (3) Derive an expression for the steady state concentration of formaldehyde, H2CO, in terms of CH4, OH, rate constants, and photolysis rate coefficients. Assume the following reactions control the formaldehyde mixing ratio.

CH4 + OH → H2O + CH3  1

CH3 + O2 + M → CH3O2 + M† 2

CH3O2 + NO → CH3O + NO2 3

CH3O + O2 → H2CO + HO2 4

H2CO + h → H2 + CO 5a

→ HCO + H 5b

2. (3) What is the *overall* lifetime, in seconds, of hydroperoxy radicals in the polluted troposphere where [O3] is 100 ppb and [NO] is 20 ppb? Repeat the calculation for the clean troposphere where [O3] is 30 ppb and [NO] is 0.002 ppb. Use the following reactions and rate constants.

HO2 + NO → NO2 + OH k = 8.1x10-12 cm3 s-1

HO2 + O3 → 2O2 + OH k = 7.3x10-14 exp(-1275/T) cm3 s-1

3. (4) You want to determine the rate constant for the reaction between ozone and nitrogen dioxide. To do so, a chamber is filled with 30 ppm O3 in air and enough NO2 is added to bring the initial concentration to 1.00 ppm NO2. The decay of NO2 is observed as a function of time, pressure, and temperature. The data for five runs are shown on the following table.

a O3 + b NO2 → Prod.

A) Plot the data in order to prove that the reaction is second order (i.e., a = b = 1). Hint: think about the pressure dependence of a third order reaction. If the reaction proceeds with first order dependence on the molecular number density of O3 and NO2, , but otherwise independent of total pressure, it's second order.

B) Express the rate constant (in appropriate units) for 298 K.

C) Write an expression for the temperature dependence.

D) Estimate the activation energy for this reaction, Ea

E) Estimate the lifetime of **NO2** in the real atmosphere with respect to this reaction.

**LABORATORY OBSERVATIONS**

**time (s) NO2 (ppm) P (atm) T(K)**

20 0.728 1.00 298

40 0.525 1.00 298

60 0.381 1.00 298

80 0.280 1.00 298

100 0.203 1.00 298

120 0.146 1.00 298

20 0.526 2.00 298

40 0.279 2.00 298

60 0.145 2.00 298

80 0.079 2.00 298

100 0.040 2.00 298

120 0.022 2.00 298

20 0.853 0.50 298

40 0.725 0.50 298

60 0.621 0.50 298

80 0.525 0.50 298

100 0.450 0.50 298

120 0.385 0.50 298

20 0.666 1.00 308

40 0.448 1.00 308

60 0.296 1.00 308

80 0.201 1.00 308

100 0.131 1.00 308

120 0.086 1.00 308

20 0.596 1.00 318

40 0.355 1.00 318

60 0.211 1.00 318

80 0.126 1.00 318

100 0.074 1.00 318

120 0.044 1.00 318

4. (2) A new, cool-burning gasoline substitute - Sprangbake - is being touted as a means of reducing NO emissions from automobiles. The only problem is that Sprangbake is about 10% (by weight) nitrogen and has a formula approximately C7H15Nx. Calculate "x" and the concentration of NO expected in the exhaust assuming complete combustion and an AFR of 16; neglect (for the moment) the Zeldovich mechanism. Express your answer in ppm, molec/cm3, and  g/m3. How does the fuel derived [NO] compare to the [NO] expected from the thermal decomposition of air during normal internal combustion?

NOTE successful completion of the quiz on the NOAA Skew-T page <http://www.meted.ucar.edu/mesoprim/skewt/table_of_contents.htm> will replace your lowest HW grade.