Analytical/Atmospheric Chemistry Cume, March 2004

R = 8.314 J mol^{-1} K^{-1} = 1.987 cal mol^{-1} K^{-1} = 0.0821 liter atm mol^{-1} K^{-1}
k = 1.38 x 10^{-23} J K^{-1}
c = 3 x 10^{8} m sec^{-1}
g = 9.8 m sec^{-2}
N_{AV}= 6.02 x 10^{23}
H at 20 km = 6.4 km
T at 20 km = 215 K
[N_2O_5] = 200 pptv at 20 km
[M] at 20 km = 1.8 x 10^{18} molecules cm^{-3}
[H_2O] = 5 ppmv at 20 km

1. The table below gives information on the photon flux at 20 km along with absorption cross section data for N_2O_5.

Wavelength interval (nm)	Photon flux at 20 km photons cm^{-2} s^{-1}	Absorption □ cm^2 $molecule^{-1}$	Dissociation quantum yield
200-205	2.5 x 10^{10}	870 x 10^{-20}	1
205-210	2.2 x 10^{10}	690 x 10^{-20}	1
210-215	5.7 x 10^{9}	465 x 10^{-20}	1
215-220	1.4 x 10^{8}	315 x 10^{-20}	1
220-225	6.5 x 10^{5}	182 x 10^{-20}	1
225-230	80	117 x 10^{-20}	1
230-235	9 x 10^{-4}	88 x 10^{-20}	1
235-240	3 x 10^{-10}	70 x 10^{-20}	1
240-260	2 x 10^{-16}	40 x 10^{-20}	1
260-280	5.4	16 x 10^{-20}	1
280-300	2.8 x 10^{12}	5.5 x 10^{-20}	1
300-320	2.15 x 10^{15}	1.2 x 10^{-20}	1
320-340	4.26 x 10^{15}	.28 x 10^{-20}	1
340-360	6.4 x 10^{15}	.06 x 10^{-20}	1
360-380	7 x 10^{15}	.01 x 10^{-20}	1

(a) Give a qualitative explanation for the change in photon flux with wavelength observed at 20 km.

(b) Use the data in the table above to estimate the lifetime of N_2O_5 with respect to photolysis at 20 km.

(c) Sketch out how you expect the photolysis rate (i.e. J value) for N_2O_5 to vary with altitude from zero to 20 km.

2. Assume that N_2O_5 reacts with water via:

$N_2O_5 + H_2O \rightarrow 2\ HNO_3$

with a second-order rate constant of $k=2 \times 10^{-21}$ cm^3 $molecule^{-1}$ sec^{-1} at 298 K.

(a) What is the approximate activation energy for this reaction?

(b) Assuming this rate constant at 20 km, what is the lifetime of N_2O_5 with respect to gas phase reaction with water?

3. Recall that the pseudo-second order rate constant for a termolecular reaction can be written as:

$$k_{II} = \frac{k_0[M]k}{(k_0[M] + k\ )}$$

where k_0 and $k\infty$ are the low- and high-pressure limiting rate constants, respectively.

Consider the termolecular reaction:

$NO_2 + NO_3 + M \rightarrow N_2O_5 + M$

The equilibrium constant for this reaction can be parameterized as
$K(cm^3\ molec^{-1}) = 4.0 \times 10^{-27} \exp(10{,}930/T)$.

Assuming values of k0 and $k\infty$ of

$k0(T) = (2.2 \times 10^{-30})\{T/300\}^{-3.9}$ cm^6 $molec^{-2}$ sec^{-1}

$k\infty(T) = (1.5 \times 10^{-12})\{T/300\}^{-0.7}$ cm^3 $molec^{-1}$ sec^{-1}

estimate the lifetime of N_2O_5 with respect to thermal decomposition at 20 km.

4. Assume that N_2O_5 is taken up by sulfuric acid particles in the atmosphere with an efficiency of □=0.1.

(a) Assuming a sulfuric acid loading with a particle surface area at 20 km of SA=5 □m^2/cm^3, estimate the lifetime of N_2O_5 with respect to heterogeneous loss on the particles.

(b) Using your answers in parts 1b, 2b, 3 and 4a, what is the overall chemical lifetime of N_2O_5 at 20 km?

5. (a) Estimate the time it would take for N_2O_5 to be mixed around the Earth zonally and meridionally at 20 km if it had no chemical losses.

(b) Estimate the time it would take for N_2O_5 to be mixed vertically through one scale height at 20 km assuming an eddy diffusion coefficient of Kz=3 x 10^3 $cm^2 sec^{-1}$ at 20 km.

6. Discuss the roles of transport versus chemistry in controlling the distribution of N_2O_5 at 20 km.