**ATOC 3500/CHEM 3151 Spring 2018**

**Problem 17**

**Evaluating the importance of Heterogeneous Chemistry of N2O5**

In the lowermost stratosphere, very close to the tropopause, there is a thin layer of particles composed mainly of sulfuric acid and water (and some other more exotic compounds, including metals, organic molecules, and even small bacteria!). The surface area density of this particle layer is about 1 m2 cm-3.

After sunset (or in polar darkness), NO2 is converted into N2O5, a species that photolyzes to reform NOx (NO and NO2) when sunlight returns. However, N2O5 can also react heterogeneously, so that if the particle surface area is high enough, it can be removed before the sun reappears. This acts to remove NOx from the gas phase, which can result in an increase in reactive forms of chlorine that destroy ozone.

These reactions can be written as:

NO2 + O3 🡪 NO3 + O2

NO2 + NO3 + M 🡪 N2O5 + M

N2O5 + h 🡪 NOx (NO and NO2)

N2O5 + H2O 🡪 2HNO3

Consider the heterogeneous hydrolysis of N2O5 on stratospheric particles (the fourth reaction above). The rate coefficient for a heterogeneous reaction is typically given by k =  vA/4, where  is the reaction probability, v is the mean speed of molecules in the gas phase and A is the particle surface area. For N2O5 hydrolysis,  is about 0.1 and v is about 200 m s-1. We write the “rate” of the reaction:

Rate = d[N2O5]/dt = -  vA/4 [N2O5]

1. Calculate the rate of N2O5 hydrolysis for a particulate surface area density of 1 m2 cm-3.
2. The J-value for photolysis of N2O5 is about 1 x 10-4 s-1. What are the relative lifetimes of N2O5 with respect to heterogeneous reaction and with respect to photolysis (i.e., calculate two separate ‘lifetimes’)?

(c) Estimate the surface area density that would be required for the two ‘lifetimes’ in (b) to be about the same (i.e., so that the rate of the heterogeneous reaction is about the same as the photolysis rate).