

ATOC 3500 – Tuesday, March 15, 2011

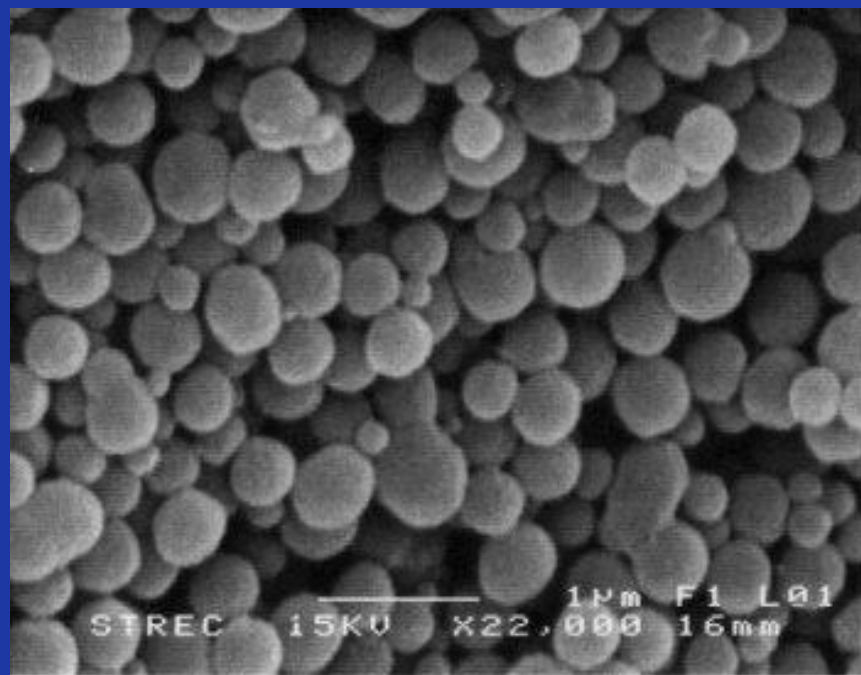
Discussion of projects (be ready to present ~ 1 page of notes – see web page – when we get back from Spring Break

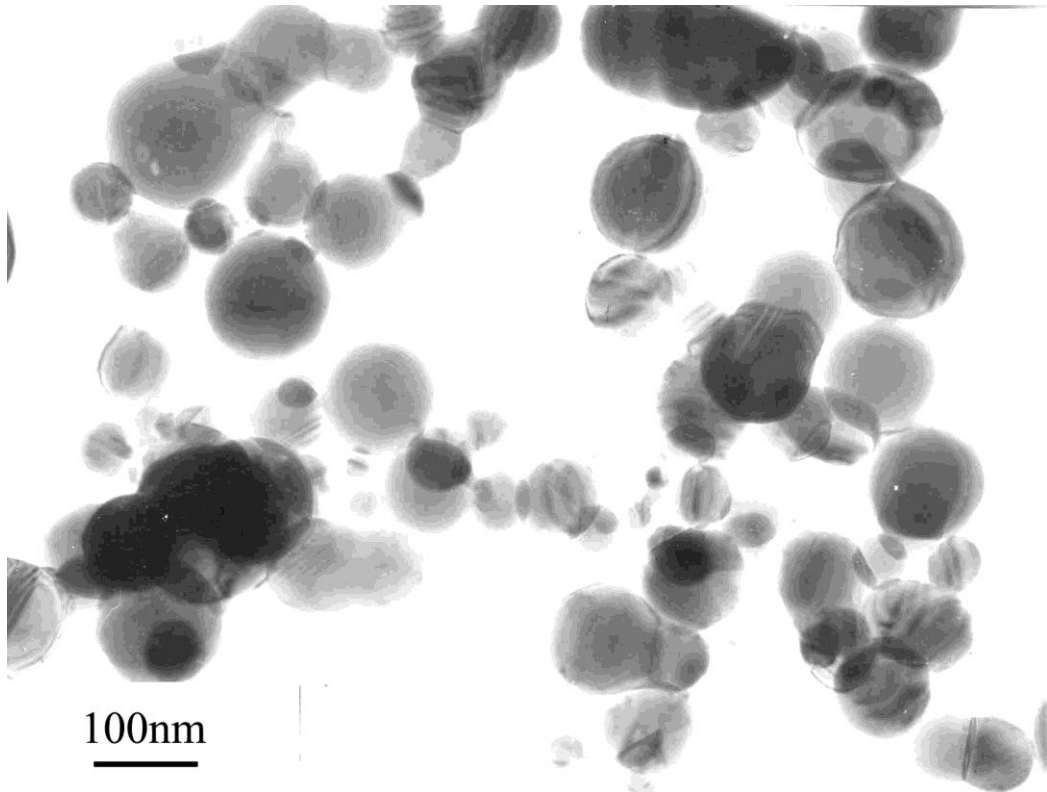
Lots of news this week, but dominated by the disaster (earthquake and tsunami) in Japan and the situation with the nuclear reactors.

Discussion of homework problems 12 and 13

The idea behind Problem 12 is to get used to the units that are used for surface area density (amount of particulate surface available for heterogeneous reactions in a volume of air). The units are a bit foreign, because we are dealing with a mixture of condensed material and a gas. We need a way to express condensed phase quantities (e.g., number of particles and amount of surface area or volume of those particles in a gas).

Here is a photo of a bunch of nanoparticles. These are packed in much closer than they would be in the atmosphere, but this gives you some idea of the nature of the problem. Each particle has a particular shape and size (these are nearly spherical), so there will be a surface area and volume associated with each particle, and there are certain number of particles in a given volume of air (in this case, LOTS!).





In the atmosphere, particles aren't so well behaved, unless they are liquids (which are typically spheres). Here is an example of some particles that aren't uniform in size and shape. It would be difficult to calculate the area and volume of a distribution of particles like this, but we would still use the same way of expressing the results. The goal of problem 12 is to practice some calculations that are typical for aerosols.

The quantities that will be most important to us will be

“total particulate surface area in a given volume of air”

“total particulate volume in a given volume of air”

To calculate these quantities, we need to know the number of particles in a given volume of air at each size (or diameter).

Surface area of a single particle = $4 \pi R^2$

Volume of a single particle = $\frac{4}{3} \pi R^3$

The “surface area density” =

“surface area of a single particle” x “number of particles in a cm^3 air”

Note – on the bottom of page 129 the book mentions a specific surface area of $3 \times 10^{-3} \text{ cm}^2$ liquid H_2O per cm^3 of air. Note how carefully the author describes the quantity – literally spelling out “there will be 1000 droplets in every cm^3 of air, and the total surface area of water will be about $3 \times 10^{-3} \text{ cm}^2$.

Note that the units will be a bit tricky to track. The dimensions for volume of a particle will be length³ and the units for the volume of air are the same. So if we aren't careful, we can end up with no units for the 'volume density' of particulate material

Example – what if we were to measure 10 μg of condensed water in a cubic meter of air? We know that 1 gram of water occupies 1 cm³. So this would correspond to 10⁻⁵ cm³ of condensed water in 1 m³ of air, or, because 1 cm = 0.01 m, this is 10⁻¹¹ m³ of condensed water in 1 m³ of air. If we just take the ratio of these values, we get

$$10^{-11} \text{ m}^3 / 1 \text{ m}^3 = 10^{-11} \text{ with NO UNITS!}$$

Now we are lost – we can't determine if this was a quantity that was volume in volume, area in area, a ratio of numbers, etc.

So the easiest way to distinguish between these two sets of dimensions is to call of them “condensed” and the other “air”

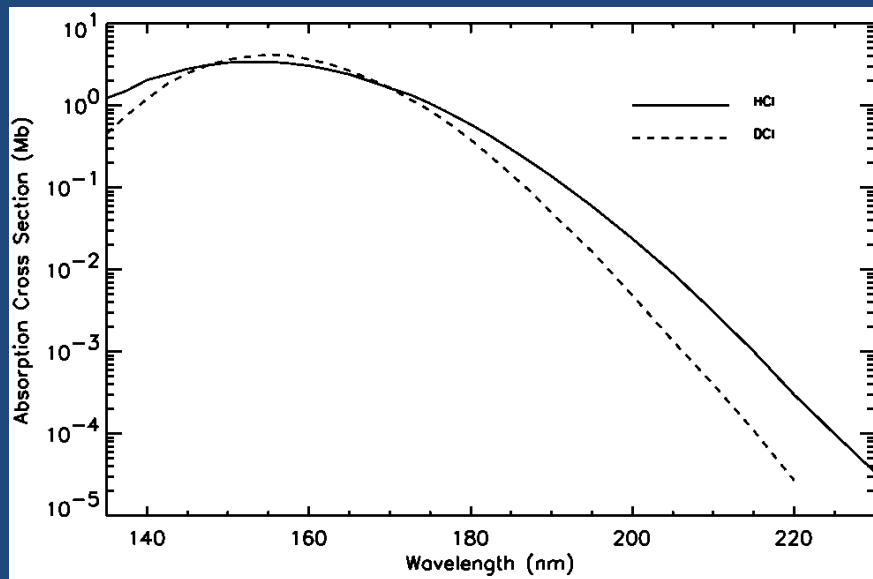
$$10^{-11} \text{ (m}^3 \text{ of water) / 1 (m}^3 \text{ of air)}$$

We can now easily tell that this is a volume of condensed material in a specific volume of air.

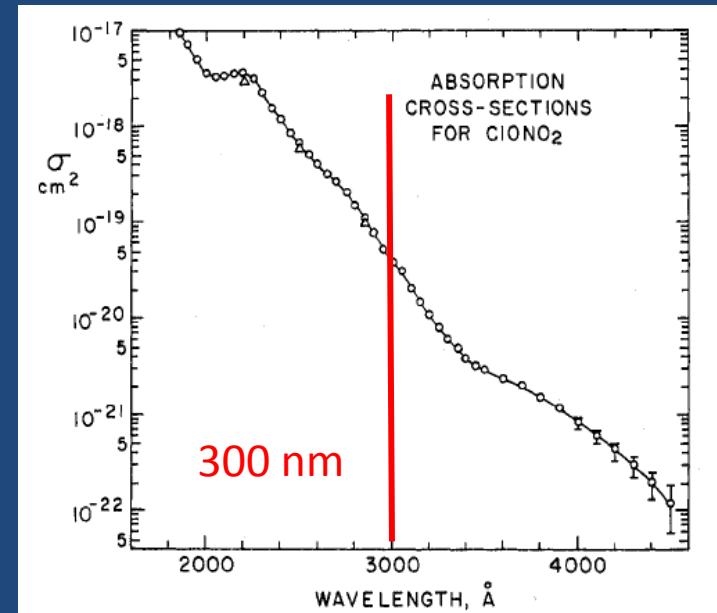
The idea for the homework is to get used to some of the units that are common in the literature. It is common to express area of particulate material in “square microns” (or μm^2) and for volume to be expressed in units of “cubic centimeters” (or cm^3). Air is usually expressed in units of cm^3 or m^3 , since there isn’t much stuff in smaller volumes of air.

Heterogeneous Chemistry (Text, p 128-136, 149-150)

Recall that the ozone hole cannot be explained without invoking a process that converts inactive forms of chlorine (HCl and ClNO_3) into a form that can photolyze in weak sunlight in Aug/Sept to produce radical forms of chlorine (and ultimately ClO). HCl and ClNO_3 do not photolyze under the dim sunlight conditions of winter/spring over Antarctica. This is because neither has an appreciable cross section at wavelengths longer than the ozone cutoff at 300 nm.



HCl Absorption Cross Section



ClONO_2 Absorption Cross Section

In addition, the rate constant for the reaction of HCl with ClONO_2 in the gas phase is immeasurably small, $k < 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

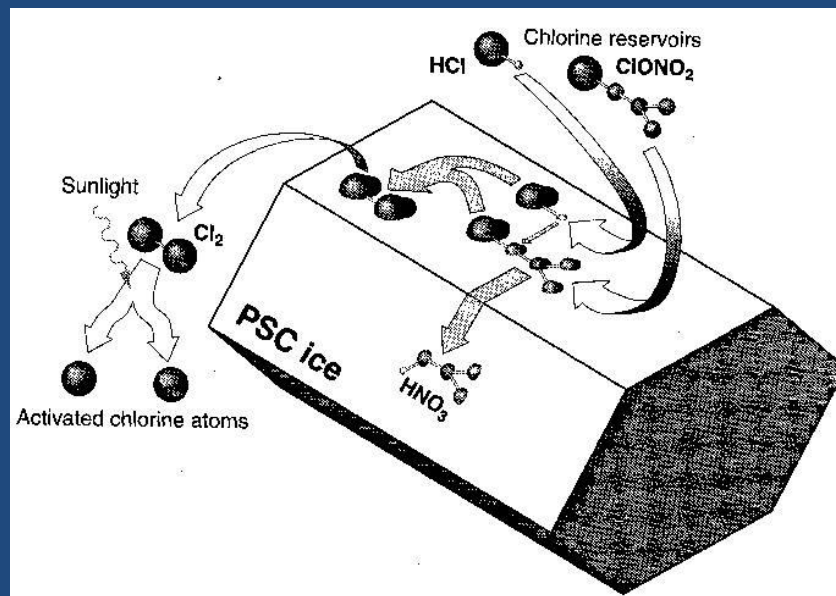
Thus, for an HCl mixing ratio of 2 ppb (at an air density, $[M]$, of $2 \times 10^{18} \text{ molecules cm}^{-3}$), the lifetime of ClONO_2 can be estimated:

$$\begin{aligned} \text{Rate} &= k [\text{HCl}] [\text{ClONO}_2] < 10^{-20} \times (2 \times 10^{18}) \times (2 \times 10^{-9}) \times [\text{ClONO}_2] \\ &= 2 \times 10^{-11} [\text{ClONO}_2] \end{aligned}$$

$$\text{So } \tau_{\text{ClONO}_2} = [\text{ClONO}_2] / 2 \times 10^{-11} [\text{ClONO}_2] = 5 \times 10^{10} \text{ s} = 600,000 \text{ days} = 1600 \text{ years!!!}$$

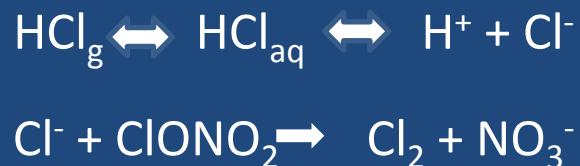
So under normal conditions, HCl and ClONO_2 aren't going anywhere!

So what happens when these two species hit a surface that is wet (or made of ice)?



The mechanism for this reaction on ice (or liquid droplets) is uncertain, but it most certainly involves charge separation in the molecules.

HCl prefers to be $\text{H}^+ + \text{Cl}^-$ in solution, so what most likely occurs is that Cl^- reacts to form Cl_2 , which is a gas, so it comes off in the vapor phase, leaving NO_3^- in solution (aq = aqueous):



This process occurs very rapidly in solutions at low temperatures. The net reaction is



Rate constants for heterogeneous reactions are more complex than those for reactions in the gas phase. We need to know a few things about the particles and the nature of the interaction between gases and particles in order to calculate the rate at which a molecule will react with another molecule once it hits the surface.

$$\begin{aligned} \text{Rate} &= (\text{collision rate with surface}) \\ &\quad \times (\text{probability that a molecule will stick to surface}) \\ &\quad \times (\text{amount of surface area on a particle for reaction}) \\ &\quad \times [\text{HCl}] \times [\text{ClONO}_2] \\ &= k_{\text{het}} \times [\text{HCl}] \times [\text{ClONO}_2] = k'_{\text{het}} [\text{ClONO}_2] \end{aligned}$$

$$k'_{\text{het}} = k_{\text{het}} [\text{HCl}] = \frac{1}{4} c \gamma A$$

Where c = mean velocity of reactants (also written as v , for velocity), γ is the sticking coefficient (a value that can vary from 0 to 1), and A is the surface area concentration (e.g., cm^2 of particulate per cm^3 of air).

Note the form of this expression:

$$\text{Rate} = -d[\text{ClONO}_2]/dt = k_{\text{het}} \times [\text{HCl}] \times [\text{ClONO}_2] = k'_{\text{het}} [\text{ClONO}_2]$$


$$k'_{\text{het}} = k_{\text{het}} [\text{HCl}] = \frac{1}{4} c \gamma A$$

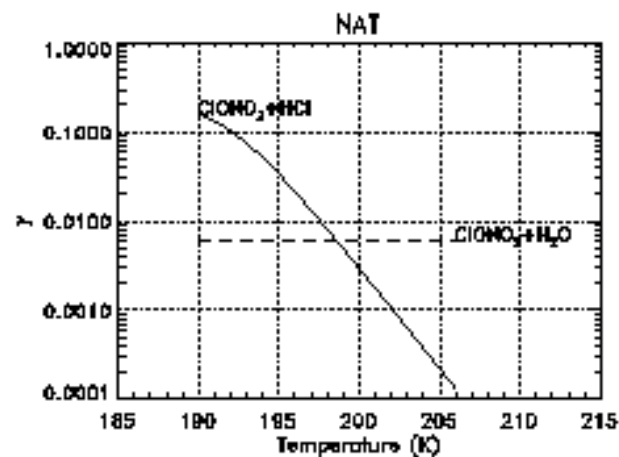
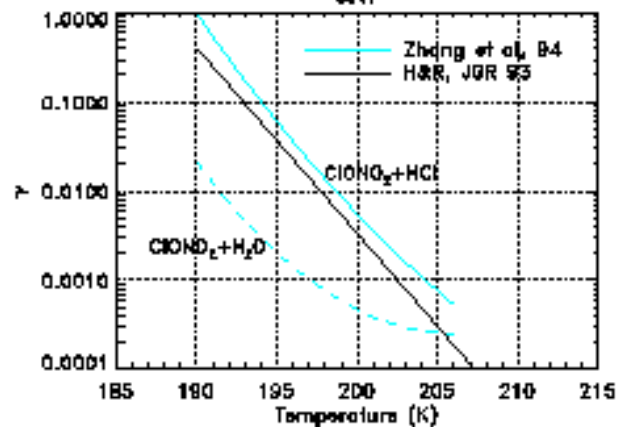
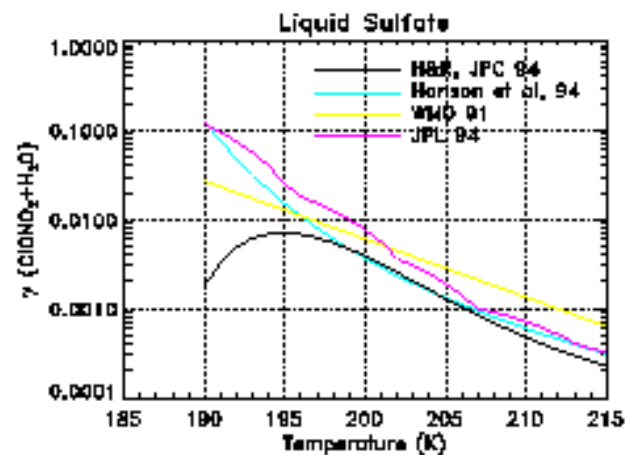
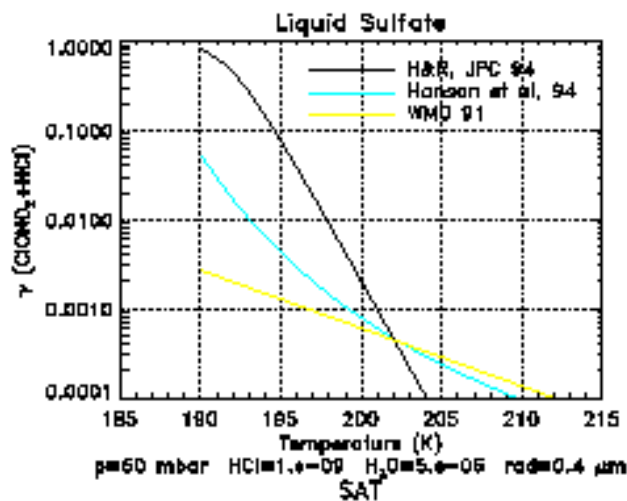
$$\text{Lifetime of ClONO}_2 = [\text{ClONO}_2] / \text{Loss rate of ClONO}_2$$

$$= [\text{ClONO}_2] / k'_{\text{het}} [\text{ClONO}_2]$$

$$= 1 / k'_{\text{het}}$$

So k'_{het} will be in units of inverse seconds.

This figure shows some results of laboratory studies of the sticking coefficient for this reaction on three types of particles – sulfuric acid (sulfate), sulfuric acid tetrahydrate (frozen sulfuric acid), and nitric acid trihydrate (frozen nitric acid). These are materials that are similar to those found in the Antarctic and Arctic stratospheres in winter. Note that at temperatures below 196 K, gamma exceeds 0.01. This value will turn out to be very important.



Let's look at the implications of this heterogeneous reaction on converting HCl and ClNO₃ into more reactive forms if $\gamma = 0.0001$ (the value found in the laboratory for T~210 K for all three types of stratospheric particles).

The approximate velocity of a molecule is $(3RT/M)^{1/2}$, where M is the molecular weight, R is the universal gas constant, and T is in Kelvin. This works out to be about 200 m s⁻¹ for HCl at 200 K (a pretty easy number to remember).

$$k'_{\text{het}} = 0.25 \times 0.0001 \times (200 \text{ m s}^{-1}) \times A$$

In Homework Problem 12 you calculated that the typical surface area density, A, for stratospheric aerosol.

$$\begin{aligned} k'_{\text{het}} &= 0.25 \times 0.0001 \times (20,000 \text{ cm s}^{-1}) \times 2.8 \times 10^{-8} \text{ cm}^2/\text{cm}^3 \\ &= 1.4 \times 10^{-8} \text{ s}^{-1} \end{aligned}$$

Note that the units for k'_{het} are inverse seconds, so this allows us to estimate the lifetime for ClNO₃ as $1/k'_{\text{het}} = 7,140,000 \text{ s} = 800 \text{ days}$.

So let's go back and look at some of the implications of this quick analysis. It tells us that under normal stratospheric conditions ($T > 210$ K, normal stratospheric particle amounts), it takes over two years to convert HCl and ClNO_3 into Cl_2 . While this is certainly faster than 1600 years, it's still not going to be very important in the atmosphere – it certainly won't convert much chlorine into reactive forms in the polar stratosphere. I.e., it can't explain the ozone hole, unless something were to be different in our calculation.

Well, we already know that it's important in the ozone hole. So how is this possible? Last week we saw ClO abundances jumped significantly when temperatures dropped below about 198 K. At these temperatures, the sticking coefficient we should use is 0.01 or larger, that is, 100 times larger than the value we used for the 'normal' stratosphere. This will reduce the lifetime of ClNO_3 to 8 days! Winter over the poles lasts about 3 months, so this is plenty of time to convert the HCl and ClNO_3 into Cl_2 . In fact, this change alone is enough to explain how chlorine can be 'activated' into forms that destroy ozone over the long, cold winter over both poles.

In addition, when temperatures drop below 200 K, ice crystals made up of water and nitric acid begin to form. This further enhances the surface areas of particles, further reducing the lifetime of ClNO_3 to less than a day. Therefore, it only takes a few days in winter for these heterogeneous reactions to convert HCl and ClNO_3 into Cl_2 , a molecule that readily photolyzes into Cl atoms when sunlight returns to the polar regions in springtime.