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Mass Accomodation Coefficient Measurements for HNO_3, HCl and N_2O_5 on Water, Ice and Aqueous Sulfuric Acid Droplet Surfaces

Doulgas Worsnop, Mark Zahniser and Charles Kolb
Aerodyne Research, Inc., 45 Manning Road, Billerica, MA 01821

Lyn Watson, Jane Van Doren, John Jayne and Paul Davidovits
Department of Chemistry, Boston College, Chesnut Hill, MA 02167

We report preliminary results of the direct measurement of accommodation coefficients for HNO_3, N_2O_5 and HCl on water drops, aqueous sulfuric acid drops and ice particles. The heterogeneous chemistry of these species together with $ClONO_2$ has been implicated in the ozone depletion observed in the antarctic stratosphere during the spring in the last eight years. The most plausible chemical mechanism involves the removal of nitrogen oxide species via condensation on ice particles in polar stratospheric clouds resulting in an increase in the active chlorine species responsible for the ozone depletion. The observation of low NO_2 and high ClO densities in the antarctic stratosphere last summer appear to be consistent with such a mechanism.

This heterogeneous mechanism is also supported by ground breaking laboratory experiments at JPL (Molina et. al., 1987) and SRI (Tolbert et. al., 1987) which showed that key reactions have sufficiently large probability ($> 10^{-3}$) on ice surfaces at 200 K to be important in the antarctic stratosphere:

$$N_2O_5 + H_2O(s) \dashrightarrow 2HNO_3(s)$$

$$ClONO_2 + H_2O(s) \dashrightarrow HOCl(g) + HNO_3(s)$$

$$ClONO_2 + HCl(s) \dashrightarrow Cl_2(g) + HNO_3(s)$$

These reactions have the net effect of freeing active chlorine and removing odd nitrogen in the form of condensed nitric acid. However, because gas phase diffusion limits the rate of mass transport to the macroscopically large surfaces used in these experiments, many of the details of the surface reaction kinetics were unresolved in these first experiments. Furthermore, the combination of laboratory gas densities that are much larger than those in the atmosphere and the long gas/surface contact times (> 0.1 sec) may lead to surface saturation effects that are not representative of atmospheric conditions. There is also a need to extend heterogeneous reaction studies to sulfuric acid surfaces which are characteristic of global stratospheric aerosols.

Our experimental technique can directly measure heterogeneous uptake rates of gases corresponding to accommodation coefficients from 10^{-4} to 0.3 and larger. A measured flow of trace gas is exposed to a fast moving (20 meter/s) stream of droplets. The droplet stream provides a continuously renewed surface of well defined area. Depletion of trace gas is measured as a function of surface area to which the gas is exposed. Although laboratory gas densities are still larger than in the stratosphere, the potential for surface saturation effects is reduced by limiting the time of contact between the surface and trace gas to a millisecond or less. Operation at low pressure (down to 2 torr) and the use of small droplets (100 μm) maximizes gas phase diffusion rates. Furthermore, gas phase mass transport rates can be deconvoluted from surface kinetics by varying the carrier gas pressure and composition.

Figure 1 shows a schematic of the apparatus. A stream of regular droplets is generated by pressurizing the liquid above a 60 μm orifice vibrated with a piezoelectric crystal. The size, spacing and velocity of the droplets are monitored with a cylindrically focussed He/Ne laser beam. The droplet stream is passed through two vacuum chambers before transversely crossing a 2.5 cm diameter flow tube. The stream is collected in a temperature controlled flask in a separate chamber. The composition of the atmosphere in each vacuum chamber is carefully controlled in order to maintain equilibrium between droplet temperature and water vapor pressure in the flow tube. The concentration of trace gas in the flow tube is monitored via diode laser absorption in a multiple pass cell downstream of the droplet stream.

Accommodation coefficients are calculated by comparing observed gas uptake ($\Delta n/n$) with the number of collisions of trace gas molecules with droplet surface as

$$\gamma = \frac{4F_g}{\bar{c}\ N\ A_d} \left(\frac{\Delta n}{n}\right)$$

where $\bar{c}$ is the trace gas average thermal velocity, F_g is the carrier gas volume rate of flow, and N and A_d are the number and surface area of droplets to which the trace gas is exposed.

Figure 2 plots the uptake rate, expressed as an observed accommodation coefficient, for HNO_3 as a function of the water vapor pressure in the flow tube. The variation in the water vapor pressure corresponds to a variation in the water droplet temperature, since the droplets actively cool by evaporation as they come into equilibrium with the ambient water vapor. This effect is shown in Figure 3, which plots accommodation coefficient versus inverse temperature.

The observed accommodation coefficients plotted in Figure 2 is a convolution of the "true" accommodation coefficient and the rate of gas phase diffusion of the trace gas to the droplet surface. The latter also varies as the flow tube pressure is changed. In extensive experiments with H_2O_2 and SO_2, in which the pressure was varied from 2 to 50 torr with up to 70% added He or Ar, the pressure dependent gas mass transport and heterogeneous uptake rates were deconvoluted from one another. Figure 3 plots actual accommodation coefficients obtained by correcting observed uptake rates for gas diffusion limitations using parameters determined in the H2O2 and SO2 experiments.

The line in Figure 3 shows a simple Arrhenius fit to the observed temperature dependence. The curve in Figure 2 is a convolution of this Arrhenius dependence with gas phase diffusion to simulate the actual laboratory data. The Arrhenius fit is somewhat qualitative but does give the first indication of the temperature dependence of the gas/water accommodation process.

The γ(0°C) and ΔE values obtained so far are summarized in Table 1. The negative ΔE for H_2O_2 and HNO_3 are consistent with attractive sticking of these molecules to the aqueous surface. The magnitude of ΔE in the 4-10 kcal/mole range is consistent with attractive well which is less than the solvation energy of these highly soluble species.

As listed in Table 1, we have also measured the N_2O_5 sticking coefficient to be 0.08 at 0°C. The HNO_3 and N_2O_5 results are consistent with the values $> 10^{-3}$ reported for these molecules on 200°K ice surfaces.

In experiments with pure water droplets, there is no indication that droplets freeze even upon supercooling down to -20°C. However, upon the addition of pseudomanas syringel, a naturally occurring bacterium that is known to indicate ice nucleation at -3 to -5°C, droplets freeze on a 10 millisec timescale when supercooled to -10°C. Freezing is detected via depolarization of a polarized He/Ne laser beam backward scattered from the ice particles. Preliminary experiments measured an uptake rate for HCl on to ice consistent with an accommodation coefficient of ~0.1. Uncertainties in the trace gas/stream interaction volume limit the precision of the gas/ice experiments to date, but the measured HCl uptake is consistent with that observed for other soluble gases on pure water droplets and with observations reported for ice coated surfaces (Molina et. al., 1987). Further experiments on ice particle streams are in progress.

We have also demonstrated that we can produce streams of aqueous sulfuric acid droplets up to 95% (by weight) H_2SO_4. Control of these streams is complicated by the fact that evaporation or condensation of water vapor from or to the droplets changes both the temperature and composition of the droplet surface. Preliminary experiments with HNO_3 indicate that for 50% H_2SO_4 surfaces, $\gamma(HNO_3)$ is 0.1. This is similar to the γ on pure water and is significantly larger than the $< 10^{-3}$ value typically for 95% H_2SO_4 surfaces. Further experiments are currently in progress to directly probe the range around 75% H_2SO_4 composition that is typical of stratospheric conditions.

References

Molina, M.J., T.L. Tso, L.T. Molina and F.C.Y. Wang, Science 238, 1253 (1987).

Tolbert, M.A., M.J. Rossi, R. Malhotra and D.M. Golden, Science 238, 1258 (1987).

Table 1 - Mass Accommodation Coefficients on Liquid Water Droplets

	γ(0°C)	ΔE (kcal/mole)
HNO_3	0.16	-10
H_2O_2	0.21	-4
N_2O_5	0.08	---
HCl on ice	~0.1	---

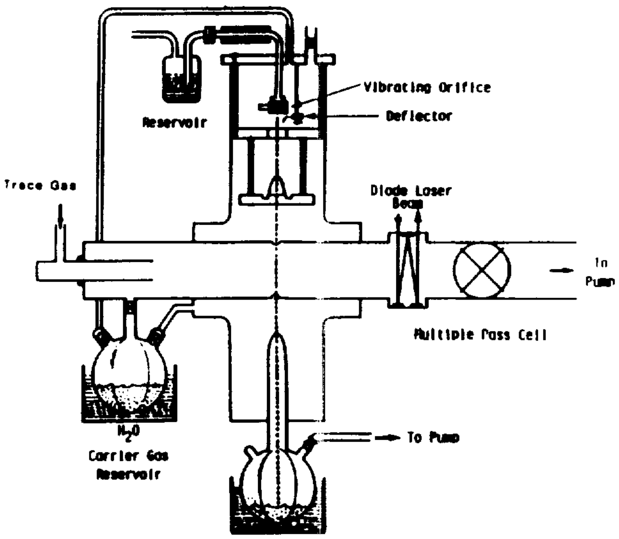

Figure 1. Experimental Apparatus for Mass Accomodation Coefficient Measurements

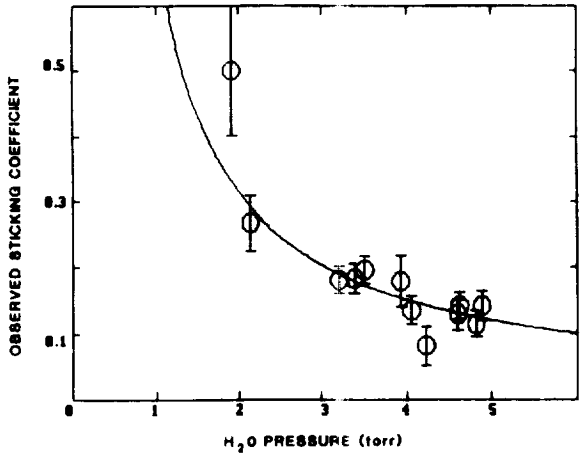

Figure 2. Observed γ Versus Water Vapor Pressure for HNO_3.

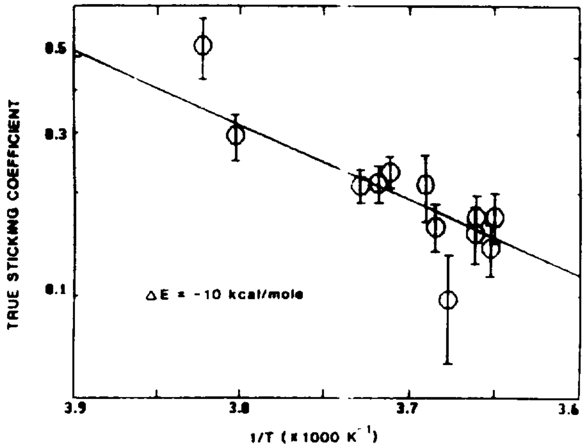

Figure 3. Semi-log Plot of Corrected Mass Accommodation Coefficient Versus 1/T.