

Mass Accommodation and Surface Reaction of NH₃ on Aqueous and Concentrated Sulfuric Acid Droplets

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Gas phase reactions involving NH₃ are slow. Tropospheric lifetime for reaction with OH radical for example, is ~2.5 months. As a result heterogeneous chemistry of NH₃ plays an important role in determining the fate of the species in the atmosphere. Since ammonia is the only soluble base found in the atmosphere in significant quantities it plays a principal role in neutralizing acidic aerosols (H₂SO₄, HNO₃ and HCl) converting them to new non-volatile aerosol particles; (NH₄)₂SO₄ NH₄HSO₄. This process of neutralization influences the aqueous oxidation rates of S(IV) species and the formation of new aerosols

Interactions of gas phase ammonia with aqueous and sulfuric acid droplets were studied under the following conditions:

- (a) The liquid water studies were done as a function of pH (0 to 12) and temperature in the range 20°C to -10°C.
- (b) The sulfuric acid studies were done in the range 10 to 70 weight percent H₂SO₄ and as a function of temperature in the range 20°C to -25°C.
- (c) Co-deposition studies were conducted in which an aqueous surface, initially at pH4, was simultaneously exposed to both gas phase NH₃ and SO₂ were also performed.

Apparatus and Experimental Procedure.

Gas uptake is measured by passing a controlled train of fast moving droplets (120-250 μm in diameter) through a low pressure (4-20 Torr) flow reactor which contains the gas phase ammonia at a density of about 10^{13} cm^{-3} , entrained in a flowing carrier-gas of water vapor and helium. The surface area of the droplets passing through the flow tube is changed in a step-wise fashion and the ammonia gas signal is monitored either with a mass spectrometer or by absorption of infrared light produced by a diode laser. The experimental results yield the uptake coefficient γ_{meas} defined as

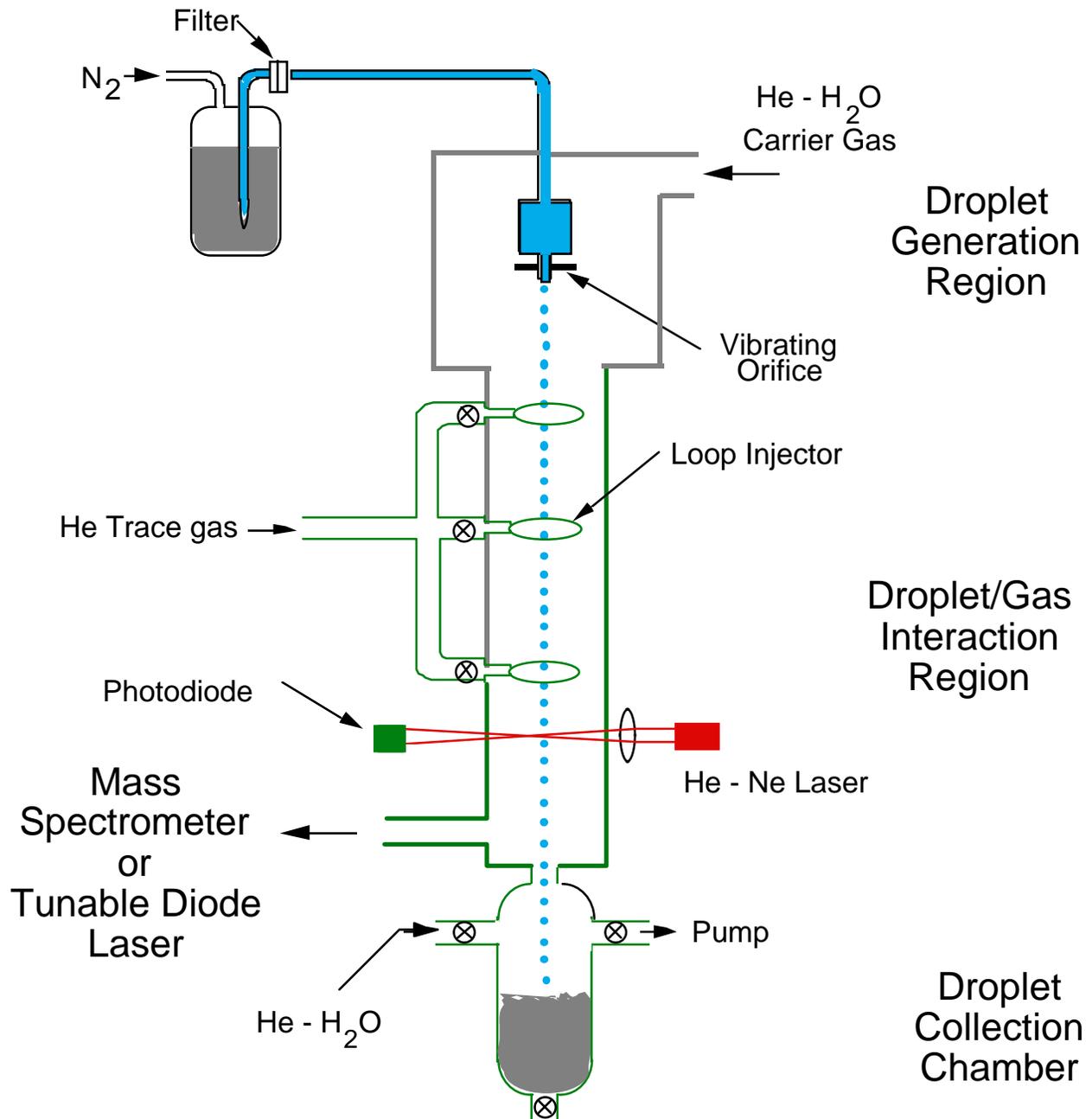
$$\gamma_{\text{meas}} = \frac{\text{Number of molecules lost to the surface (s}^{-1}\text{)}}{\text{Number of gas-surface collisions (s}^{-1}\text{)}}$$

The time dependence of the uptake coefficient is determined by measuring the uptake as a function of gas-droplet interaction time which can be varied from 2 to 20 ms by selecting the gas inlet port and by varying the droplet velocity.

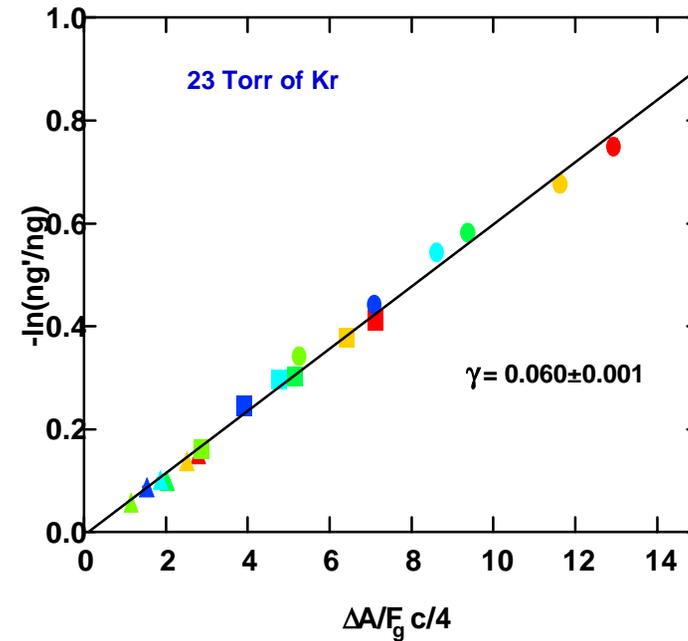
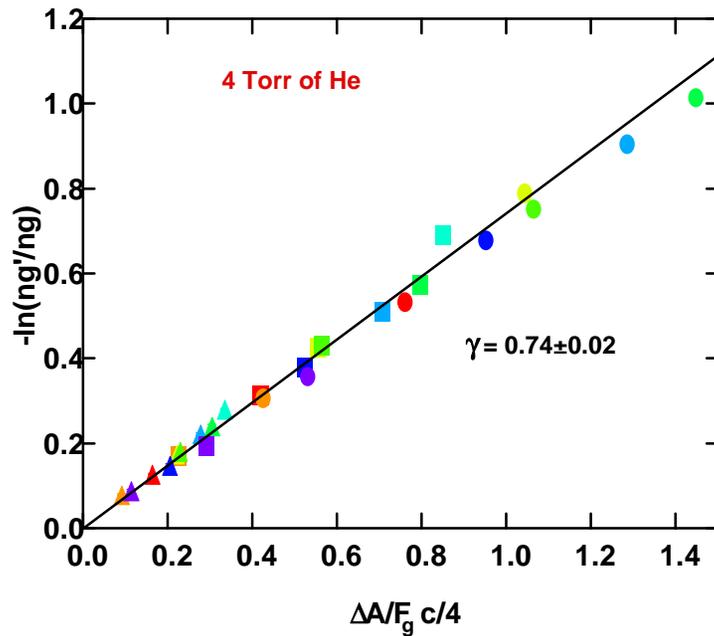
The experimental results yield information about:

- mass accommodation probability
- gas and liquid diffusion
- gas solubility
- aqueous reactivity
- surface reactivity
- surface complexes.

Droplet Train Apparatus



Uptake of NH₃ in 70 wt% H₂SO₄ at 250 K



Slope of line is γ_{meas}

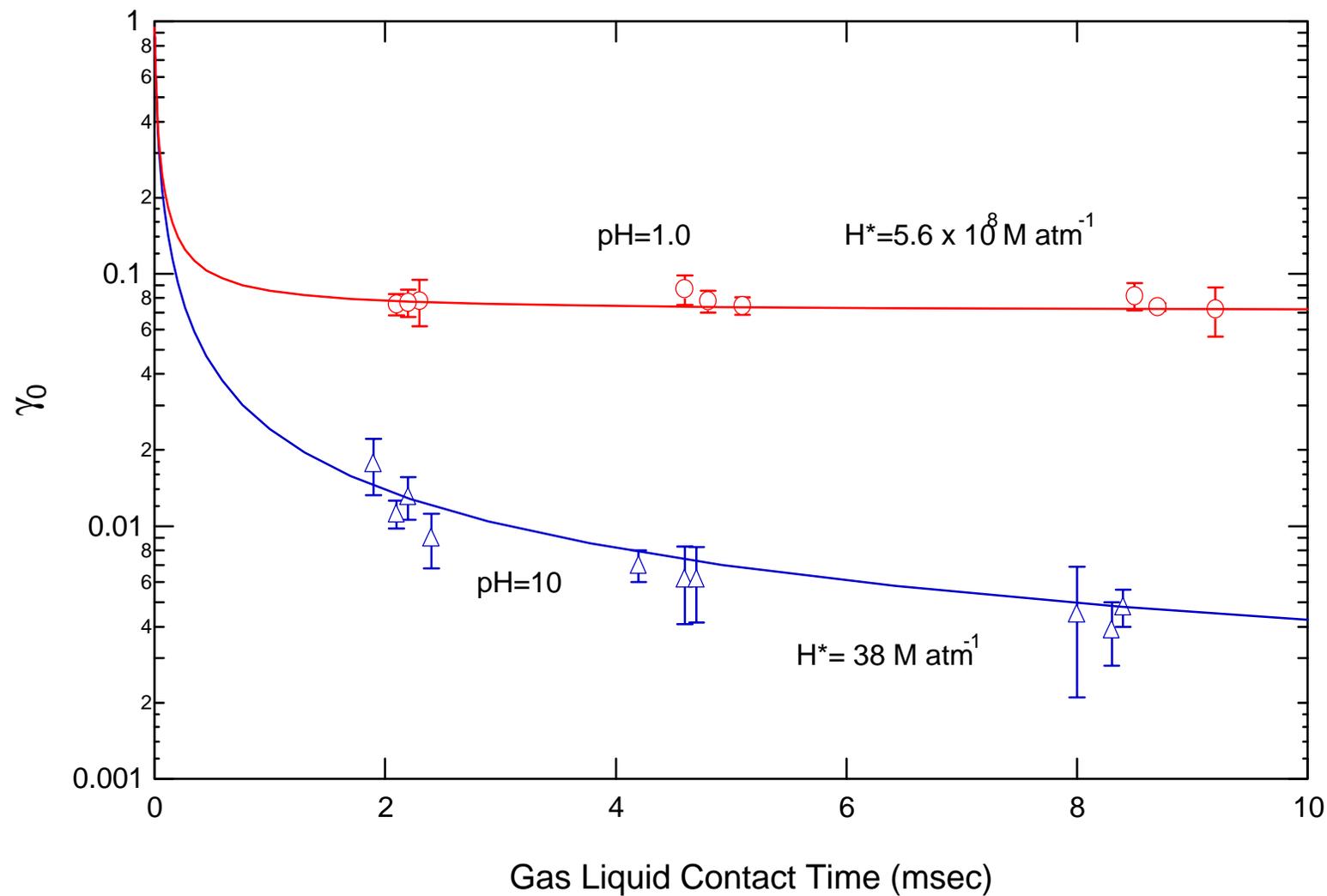
$$-\ln\left(\frac{n_g'}{n_g}\right) = \frac{\gamma \Delta A \bar{c}}{F_g 4}$$

Each color represents a different droplet diameter

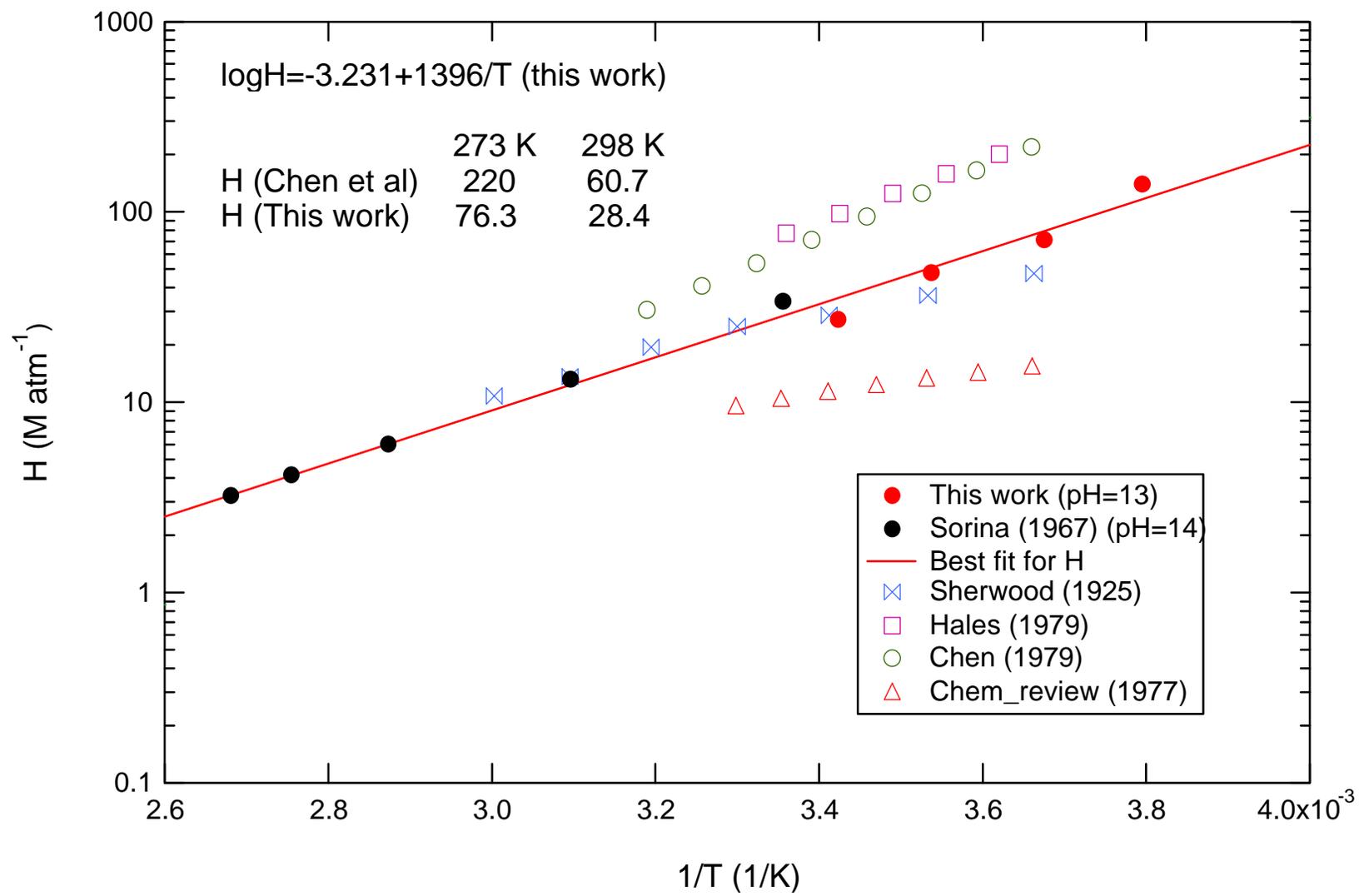
Each symbol represents a different contact time

**Uptake is linearly proportional to
Liquid Surface Area and Gas-Liquid Contact time**

Uptake Coefficient for NH₃ as a Function of Gas-Liquid Contact Time



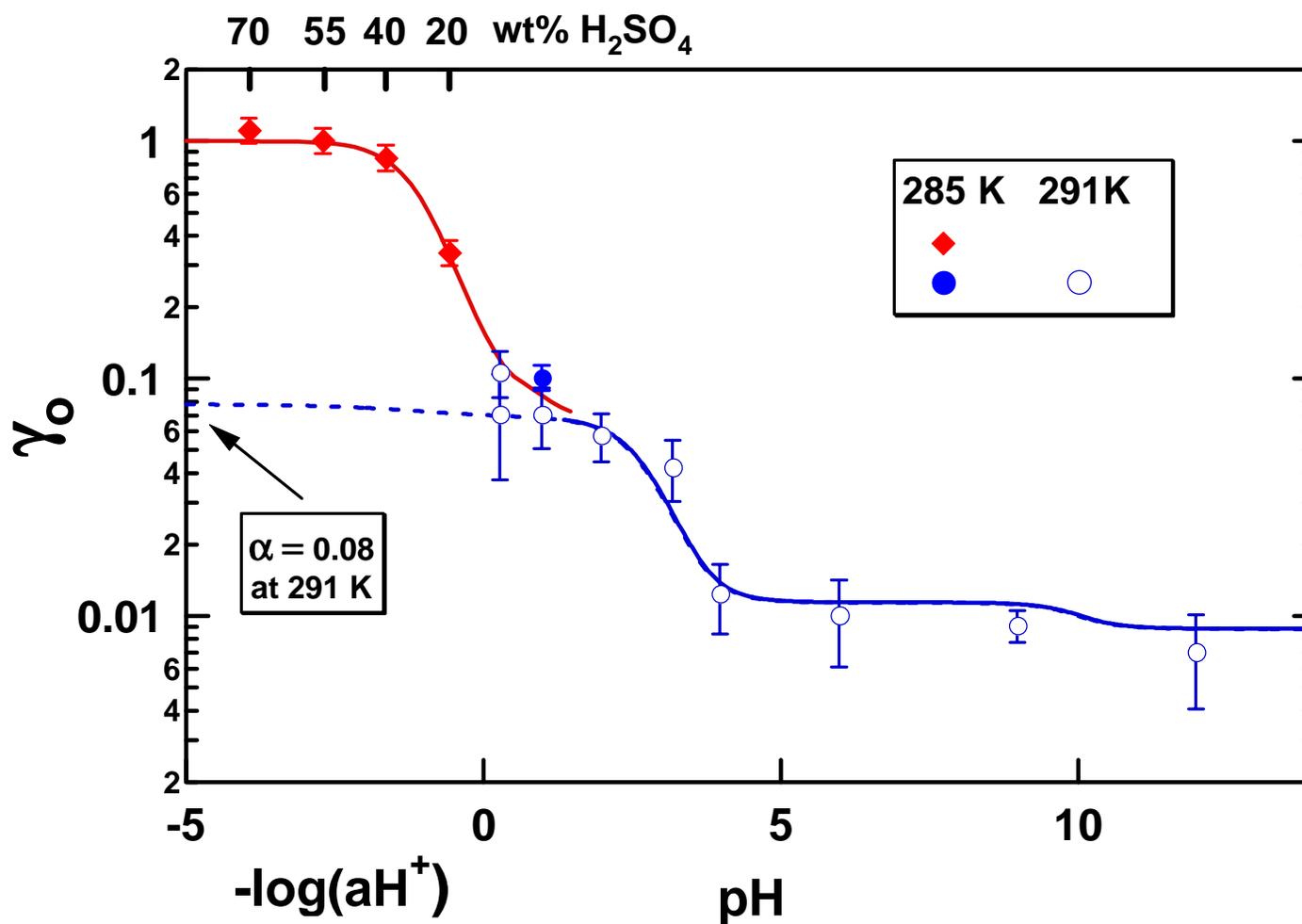
NH₃ Henry's Law Coefficient as a Function of (Temperature)⁻¹



Based on results shown in the following figures the conclusions are:

- In basic solution, ($\text{pH} > 10$) uptake is limited by physical solubility (Henry's law constant, $H \sim 100 \text{ M/atm}$), with enhanced uptake observed at $t < 10^{-2} \text{ sec}$ indicating the formation of a surface complex.
- In the region of $\text{pH} \sim 1$, uptake reflects the mass accommodation coefficient (~ 0.08 at 283K) which exhibits a negative temperature dependence consistent with a cluster nucleation model.
- Uptake increases with increasing acidity as NH_3 reacts with H^+ in solution. In concentrated sulfuric acid solutions the NH_3 uptake coefficient increases to near unity, independent of temperature, indicating the effect surface reactivity of NH_3 with H^+ . Surface reaction cross section of NH_3 with $\text{H}^+ \sim 10^{-14} \text{ cm}^2$.
- Results co-deposition studies in which an aqueous surface, initially at $\text{pH} 4$, was simultaneously exposed to both gas phase NH_3 and SO_2 are in accord with NH_3 and SO_2 bulk phase chemistry.

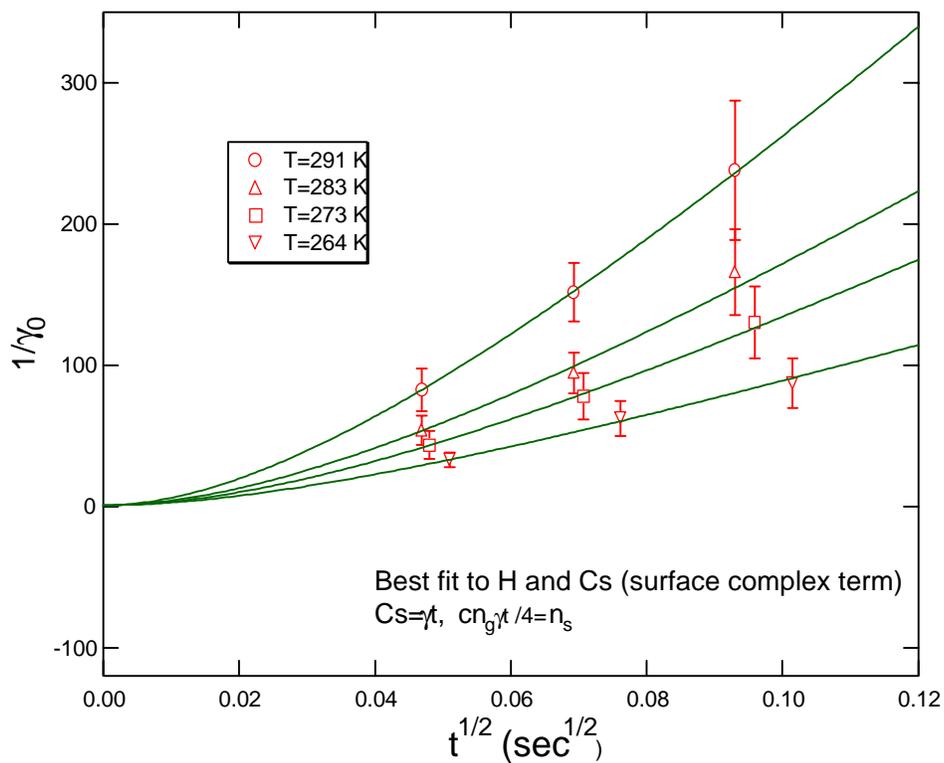
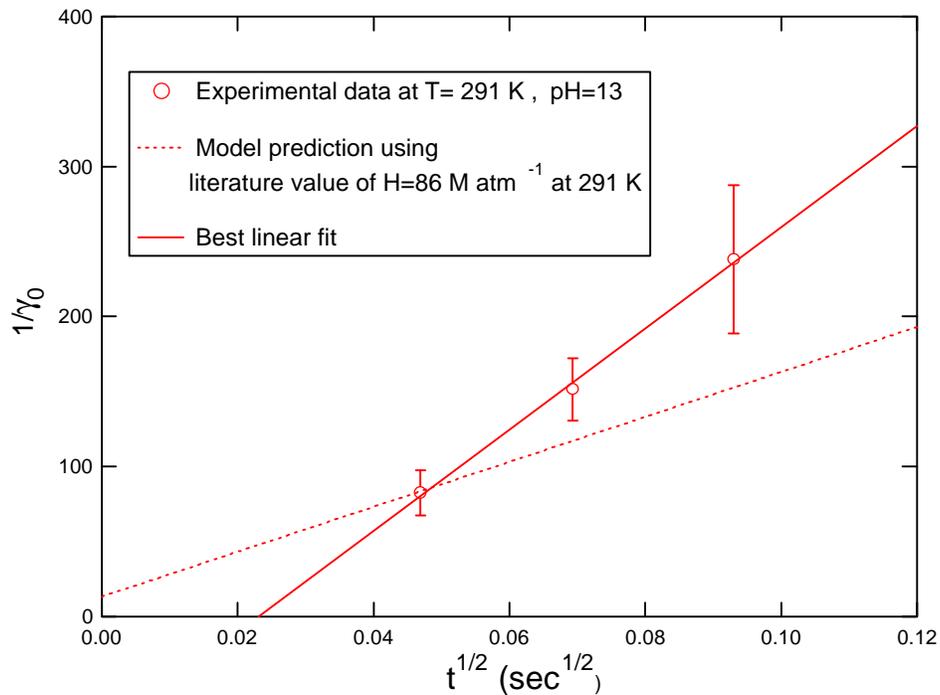
NH₃ Uptake as a Function of Droplet Acidity



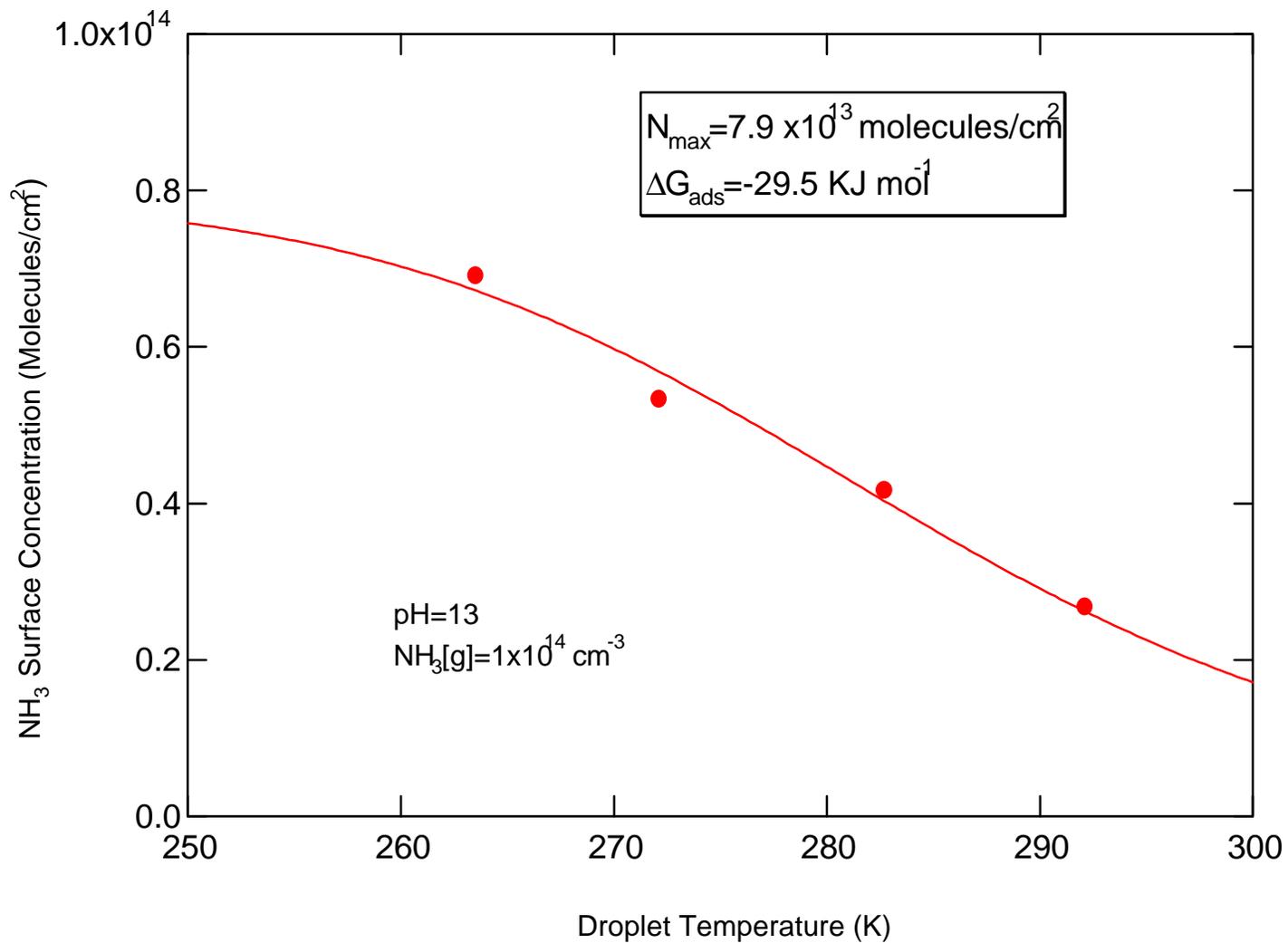
Uptake coefficient γ_0 is corrected for gas-phase diffusion.

$1/\gamma_0$ as a Function of Gas-Liquid (Contact Time)^{1/2}

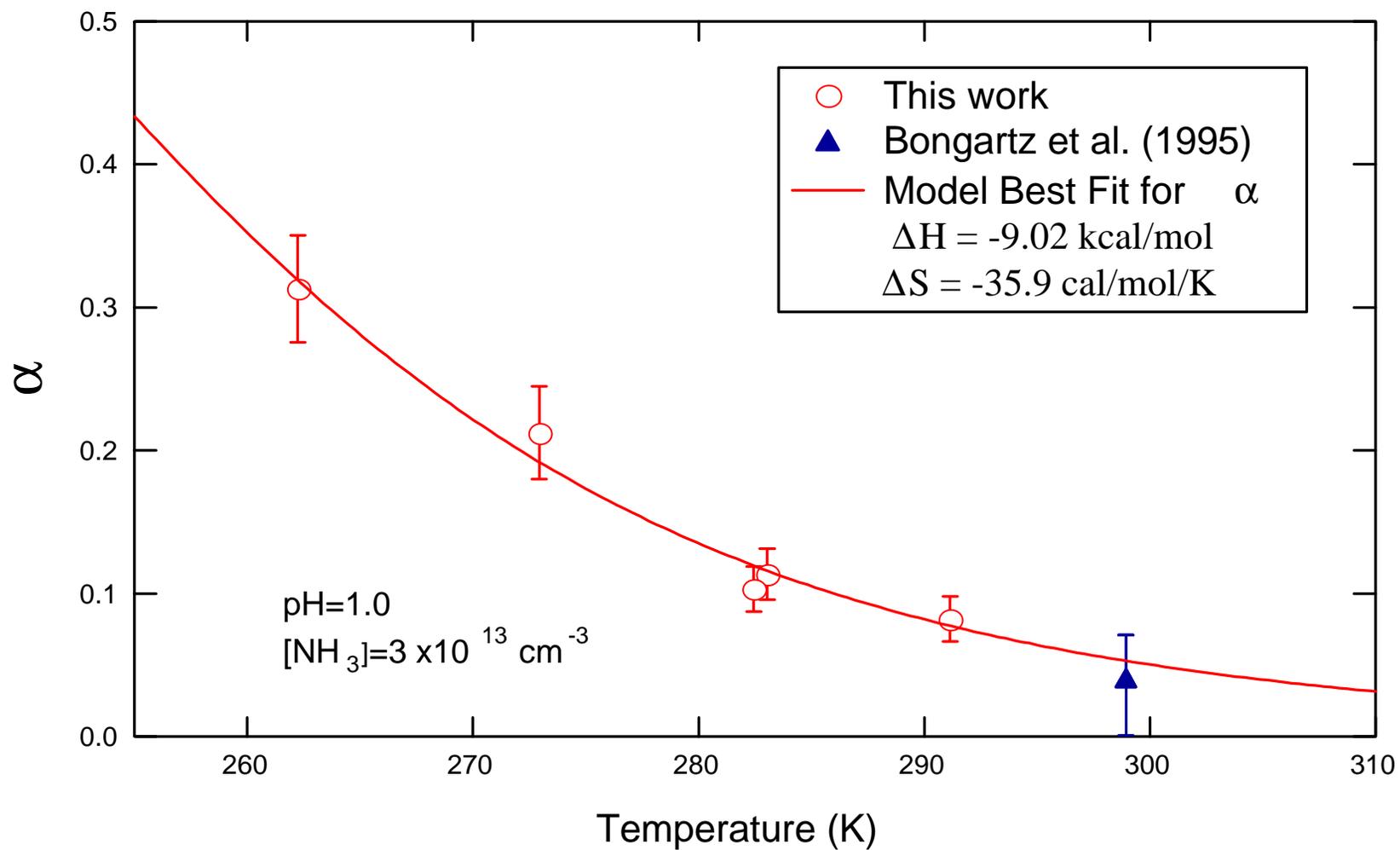
This result indicates that a surface complex is formed



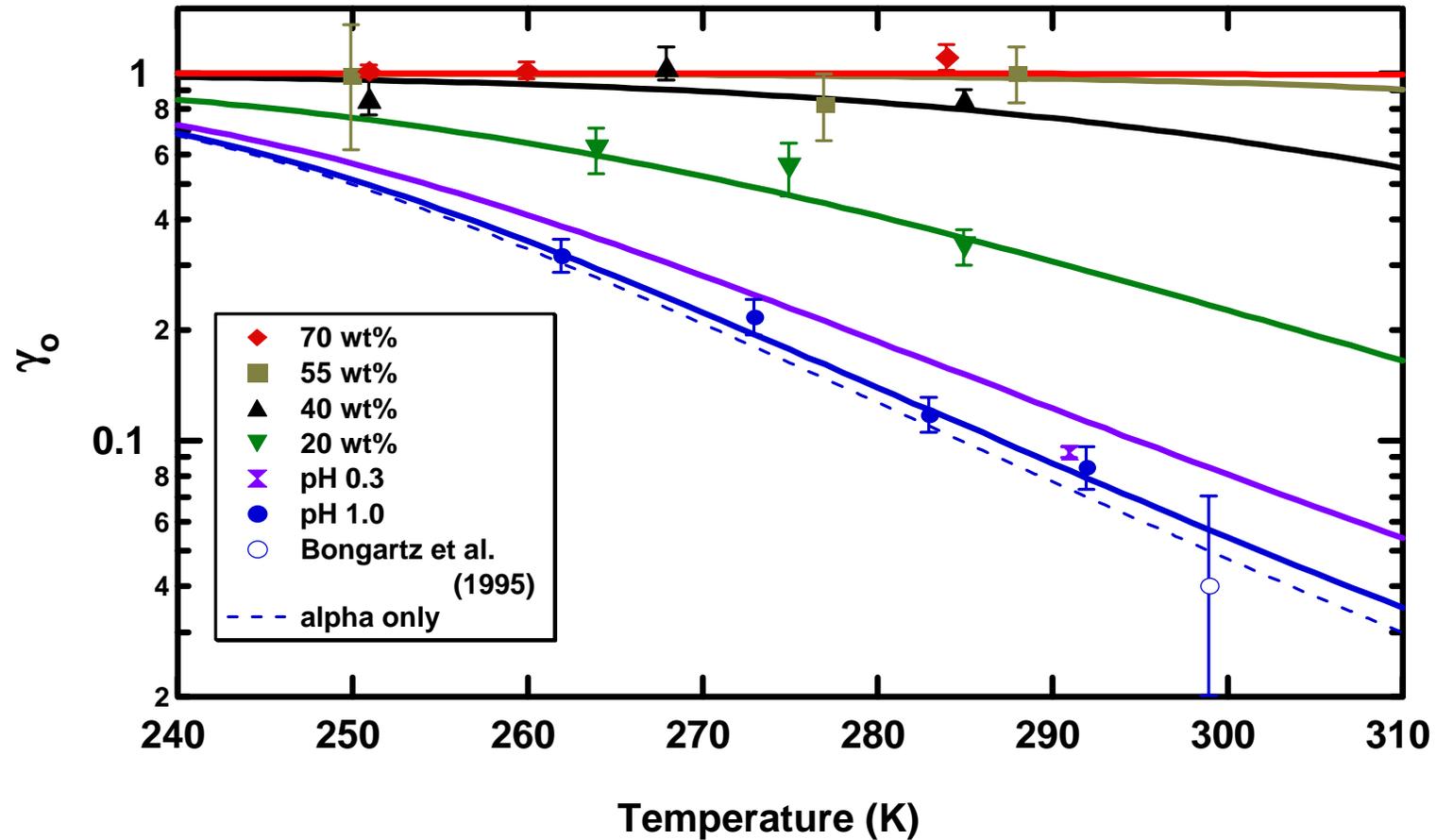
NH₃ Surface Concentration as a Function of Temperature



Mass Accommodation of NH₃ as a Function of Temperature

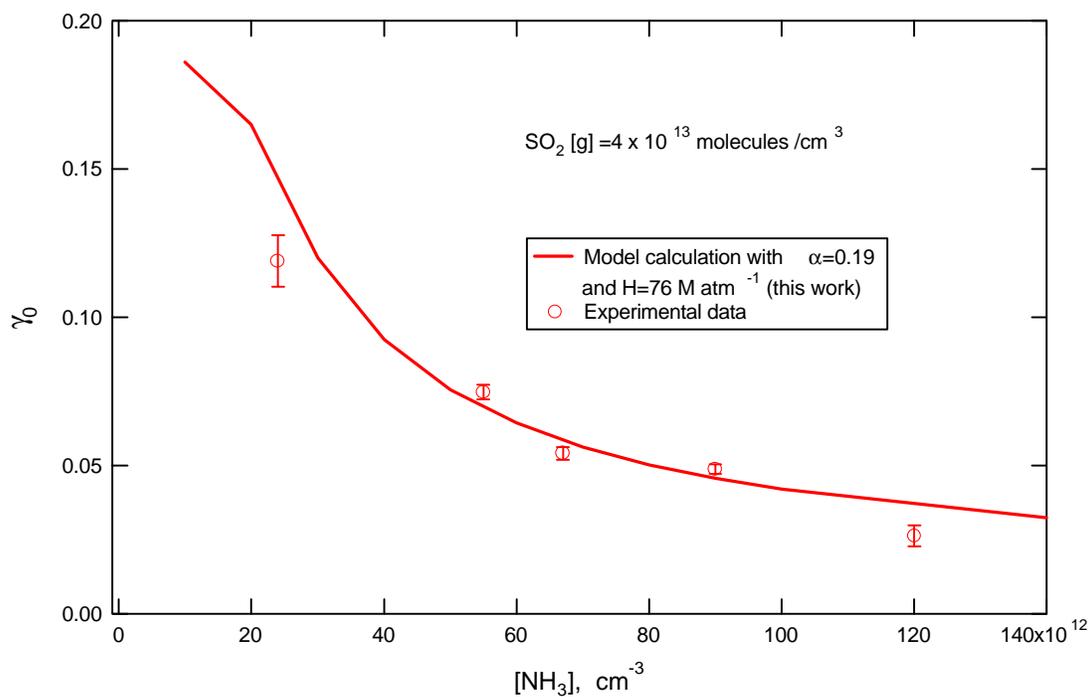
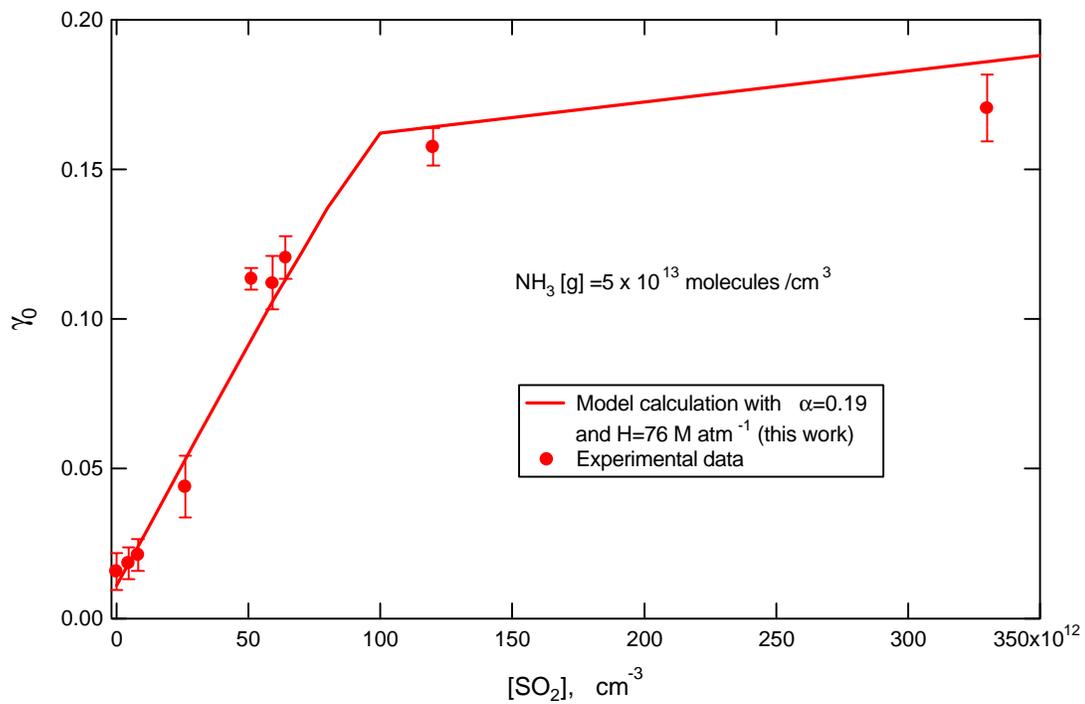


Uptake of NH_3 as Function of Temperature



This result indicates that in concentrated sulfuric acid solutions NH_3 uptake is dominated by a surface reaction of NH_3 with H^+ . Uptake coefficient $\gamma_0 = 1$.

Co-deposition Study of SO₂ and NH₃ at Droplet pH 4 and T=273 K



Atmospheric Implications

- Uptake coefficient at high concentrations of sulfuric acid is sufficiently large so that NH_3 uptake by sulfuric acid aerosols is not limited by mass accommodation but rather is determined by the gas phase collision rate.
- In the pH region greater than 0, where surface reactions are not significant, the uptake coefficient is significantly smaller than for sulfuric acid droplets, the mass accommodation coefficient α being in the range 0.07 to 0.3, depending on the temperature. Significant fraction of atmospheric aerosols is in the diameter region where mass accommodation (α) dominates the rate of uptake rather than gas phase diffusion limited transport. Therefore, a realistic attempt to model ammonia kinetics and aerosol growth in the atmosphere should take mass accommodation into account.

Gas phase diffusion

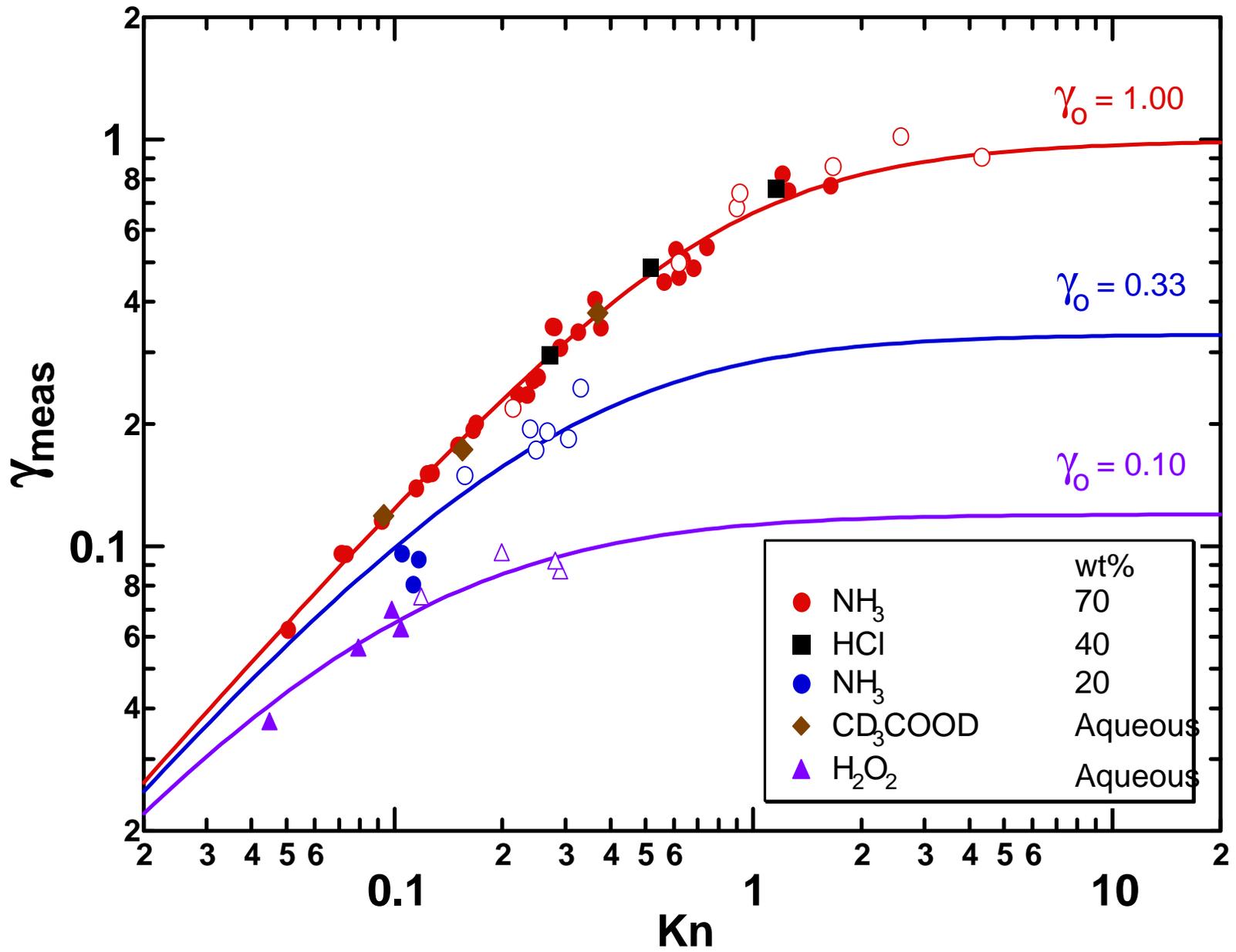
Our early experiments have shown that diffusive transport to the train of (closely spaced) moving droplets is independent of droplet diameter but depends rather on the diameter of the orifice (d), with effective diameter $d_f = (1.9 \pm 0.1)d$. Uptake was adequately described by an electrical circuit analogy with dimensionless conductances. Gas phase transport was taken into account via the expression:

$$\frac{1}{\Gamma_{\text{diff}}} = \frac{\bar{c} d_f}{8 D_g} - 1/2$$

Recently performed $\text{NH}_3(\text{g})$ and $\text{HCl}(\text{g})$ uptake measurements on sulfuric acid droplets made it possible to perform studies of diffusive transport over a wide range of Knudsen numbers up to Kn of about 4.5 with uptake coefficients ranging from 0.06 to 1. The results of these measurements confirmed the earlier findings that diffusive transport to the train of moving droplets is independent of droplet diameter. The new more extensive studies yield $d_f = (2.0 \pm 0.1) d$. The studies also showed that over the full range of Knudsen numbers and mass accommodation coefficients, gas phase diffusive transport is in accord with the formulation of Fuchs and Sutugin with $\text{Kn} = 2\lambda/d_f$, and the mean free path $\lambda = 3D_g/\bar{c}$. That is:

$$\gamma_{\text{meas}}(t) = \frac{1.333 \text{ Kn}}{1 + \text{Kn} \left\{ \left(\frac{1.333 \text{ Kn} + 0.71}{1 + \text{Kn}} \right) + \frac{4(1 - \gamma_o(t))}{3\gamma_o(t)} \right\}}$$

γ_o = uptake coefficient without gas diffusion limitation.



In the above studies Kn was varied by changing the orifice diameter and the background gas pressure.

The experiments confirmed that the simple decoupled formulation via conductance is an adequate treatment of diffusive transport in the region of mass accommodation coefficients encountered in our previous studies. The two formulations are in agreement to better than 5% up to a Knudsen number of 0.5 and $\alpha = 0.3$ (the maximum range of the earlier studies). Fuchs and Sutugin equation was used in the analysis of the current studies