Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on "Technical note: Determination of binary gas phase diffusion coefficients of unstable and adsorbing atmospheric trace gases at low temperature – Arrested Flow and Twin Tube method" *by* Stefan Langenberg et al.

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We thank the referee for reviewing and commenting our discussion paper. The remarks of the reviewer are marked like *this*. All symbols, equations and references used and cited herein refer to the discussion paper unless otherwise indicated. To the comments and questions we answer as follows:

Something in the big picture is missing: the application to the laboratory kinetics measurements whose results might depend on the accuracy of the diffusion coefficients (the stated reason for this detailed work, lines 60-62.) How will the results of these new measurement capabilities affect previously measured uptake coefficients? It seems that the ClONO$_2$ and N$_2$O$_5$ diffusion coefficients might have the most impact in this regard. A recommended set of L-J parameters for these two species would be most interesting.

Most uptake experiments with ClONO$_2$ and N$_2$O$_5$ into liquid surfaces were performed by the droplet train technique. To determine the real uptake coefficient γ_0, the measured uptake coefficient γ_{obs} had to be corrected for diffusion to the droplet surface. This can be performed by a simplistic resistance model of Hu et al. (1995)

$$\frac{1}{\gamma} = \frac{1}{\gamma_{\mathrm{obs}}} - \frac{\bar{v}r}{4D_g} + \frac{1}{2}$$

where $\bar{v}$ is the average trace gas thermal velocity and r the particle radius. The necessary diffusion coefficients were mostly taken from Hanson and Ravishankara (1991), who estimated them using the Lennard-Jones model and parameters of Patrick and Golden (1983) listed in our Table 1. In general, the investigators did not perform a sensitivity analysis of the dependency of the diffusion coefficient upon their reported γ. Therefore, it is difficult to assess, how a change of the diffusion coefficient would change the value of γ obtained.

We try to estimate this interdependency using the work of George et. al. (1994), who studied the uptake of N$_2$O$_5$ into water droplets. The dependency of the relative error of γ on the relative error of the diffusion coefficient D_g is given by

$$\frac{\Delta\gamma}{\gamma} = \frac{D_g}{\gamma}\left(\frac{\partial\gamma}{\partial D_g}\right)\frac{\Delta D_g}{D_g}.$$

Using the resistance model for a spherical particle, this yields

$$\frac{\Delta\gamma}{\gamma} = \frac{\gamma\bar{v}r}{4D_g}\frac{\Delta D_g}{D_g}.$$

George et. al. (1994) calculated the diffusion coefficient of N_2O_5 in N_2 using the method of Fuller et al. (1966). Back calculated to 273.15 K, they obtained $D_0 = 0.112$ cm^{2}s^{-1}. This value is about 24% higher than the diffusion coefficient 0.09 cm^{2}s^{-1} estimated by the LJ-model, which is consistent with our data within the error limits. At 273 K and 25.2 Torr, they obtained $\gamma = 0.020 \pm 0.002$. Assuming a particle radius of 60 μm, a diffusion coefficient of $D = 3.38$ cm^{2}s^{-1} at 25.2 Torr and $\bar{v} = 231.4$ m s^{-1}, the relative error is $\Delta\gamma/\gamma = 0.21\Delta D_g/Dg = 5\%$.

To estimate γ for the uptake of $ClONO_2$ on ice and subsequent reaction, the diffusion coefficient might be of greater importance. Hanson and Ravishankara (1992) reported for their flow tube reactor study, gas phase diffusion limits transport to the ice surface. They were only able to report an upper limit of $\gamma > 0.3$ since the diffusion coefficient of $ClONO_2$ in He was not accurately known.

We conclude that the diffusion coefficients of $ClONO_2$ and N_2O_5 calculated by the LJ-model using σ and ϵ from Patrick and Golden (1983) are a good choice. Therefore, it does not make sense to backward calculate σ and ϵ from our experimental data.

The concerns about the measurements center around these two molecules and the temperature dependencies of the D's. Both N_2O_5's and $ClONO_2$'s measured T-dependencies differ significantly from that expected for L-J interactions.

We use the `anova()` test of R (Phillips, 2018) to check if the temperature coefficient b in our Table 3 which we determined for $ClONO_2$ and N_2O_5 significantly deviates from the temperature coefficient of the LJ-model. To do this, first a fit is performed using Eq. (5) and Eq. (24) with D_0 and b fit parameters. This yields the values given in Table 3. Then the fit is repeated setting b to the value of the Lennard-Jones model. Now the

two fits (statistical models) are compared using the `anova()` test. As you can see, the T-dependencies does not differ significantly from b predicted by Eq. (7):

Species	Carrier	b	D_0	a	P	Deviation
		(LJ)	[cm^{2}s^{-1}]	[s]		
$ClONO_2$	He	1.72	0.307 ± 0.003	–	0.37	not significant
$ClONO_2$	N_2	1.88	0.086 ± 0.001	–	0.08	weakly significant
N_2O_5	He	1.73	0.31 ± 0.01	-12 ± 3	0.16	not significant
N_2O_5	N_2	1.91	0.085 ± 0.002	-29 ± 4	0.35	not significant

While losses were addressed, it seems these anomalous T-dependencies suggest there is more to the story. The indirect detection method for these two species is worth some consideration. Hard to come up with reasons why these two molecules interacting with He and N_2 should not be describable by L-J potentials.

We don't think that the titration reaction with NO can affect the temperature dependency because the titration reaction is always performed outside the thermostatted cold box in a heating zone.

Regarding the LJ-model, two things have to be considered:

1. $ClONO_2$ and N_2O_5 are both polar components with a permanent dipole moment. Therefore, the interactions with He and N_2 are not only van der Waals interactions but also dipole – induced dipole interactions. The latter are not considered in the simple LJ-model.

2. For unstable compounds like $ClONO_2$ and N_2O_5 ϵ cannot be obtained from viscosity data. ϵ can only be estimated from the boiling point using Eq. (4). But for polar component this only can be a rough estimation since the boiling point not only depends on the van der Waals interactions but also on dipole – dipole interactions.

References

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