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# *Interactive comment on* "The adsorption of nitrogen oxides on crystalline ice" *by* T. Bartels et al.

**T. Bartels et al.**

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## 1. The nature of the transport process in the column and adsorption isotherm

### 1.1. "At some point, the adsorbate of interest partitions irreversibly to the surface, and as a result a 'front' of immobilized molecules is formed."

The gas chromatographic transport of each species in the column is reversible even at low temperatures. In fact, this reversibility is mandatory to apply the chromatographic equations, as has been done successfully for many years (Eichler and Zvara, 1982; Eichler et al., 1979, 2000). For $NO_2$ the reversibility has been shown in great detail by Eichler et al. (1995), who were able to simulate the experimentally found deposition

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zone of $NO_2$ by means of a Monte Carlo simulation exclusively based on a reversible equilibrium.

**1.2. "How much would the results change for a different adsorption isotherm? (Eq. 8 implies that uptake is independent of coverage, which may be an acceptable assumption for the low coverages established in this apparatus. However, I would find it easier to accept the results if the assumption had been tested.)"**

Due to the low coverage, all chromatograms in our study show symmetric peaks, the migration distances of which are independent of partial pressure (in the range between 0.1 to 50 ppb). Both observations justify the use of linear chromatography equations. In other words, as we do not see a pressure dependence in our results, we can not apply the equations of non-linear chromatography and thus not include the effect of pressure dependence of the retention (Jönsson, 1996).

## 2. Experimental details: settings of experiments

**2.1. "The experimental data needs to be addressed very clearly and explained how/why it occurs when/where it does (e.g., NO peak adsorption at temperature T=?, $NO_2$ T=?, etc.). To this end, I recommend plotting the column temperature in Figure 2 somewhere on the x-axis. I remain somewhat confused on how the "calculated" lines were drawn on Figure 2."**

It is not the scope of this paper to investigate the molecular processes that lead to adsorption on ice and peak formation. We have mentioned the general parameters in the experimental part. The temperature at which a species is observed after an experiment, depends on the individual experimental conditions. Therefore, instead of reporting every individual deposition temperature of each species with all its associated parameters at certain experimental conditions, we prefer to report the adsorption enthalpy. The advantage is, that the latter is independent of experimental settings. For illustrative purposes, we will include the deposition temperature in Figure 2.

The calculated lines are Gaussian peak fits to our data by Origin 6.1. They are just a help to visualize the results more easily and were used to define the deposition point as the maximum of each peak.

### 2.2. "The peak desorption temperatures should also be noted"

The desorption temperature can not be evaluated with this chromatographic method.

## 3. experimental details:speculative explanations

### 3.1. "Secondly, I think more focus needs to be placed on experimental details and results,and less on speculative explanations that this experiment really can’t address (e.g.number of free OH bonds on surface, quasi-liquid layers, etc.)."

To evaluate our experiments, it is absolutely mandatory to know which processes occur in the column and determine the retention behavior. As our experimental set-up can not address the processes in the column, we used published data to evaluate which process might determine the retention. This argumentation is quite qualitative, but not speculative (in particular on the question on a quasi-liquid layer, as we actually performed experiments to evaluate its influence on our experimental results.) We are aware that this analysis is not done by all authors, but still feel that it is of fundamental importance. The importance of such analysis has nicely been shown by Huthwelker et al. (2001), who reanalyzed data of Lamb and Clapsaddle (1989), Conklin et al. (1993) and found, in contrast to the original publications, that the retention in those experiments of $SO_2$ adsorption on ice was not due to adsorption, but diffusion into the grain system of the polycrystalline ice.

## 4. experimental details: temperature gradient

### 4.1. "What is the setup for the temperature-controlled cryostat?"

We will add a figure of the apparatus's set-up to maintain a stable and negative temperature gradient to the revised version. Basically, it consists of a copper tube (10 mm i.d.), the two ends of which are kept at different temperatures. One end, from which the gas stream exits the apparatus, is immersed in liquid nitrogen. The other end is cooled with a cryostat. We used a Haake Phoenix P2-C50P thermostat or a Julabo FP88 with pure ethanol (Merck, 99 %) as cooling liquid. The cooling liquid was pumped through a copper tubing (8 mm i.d.), which was winded around the warmer end of the central copper tube bearing the ice column. The temperature gradient was stable (1 K) after 1 h of operation.

### 4.2. "Does eq. 2 require that the temperature gradient across the column be linear, and if not what would be the effect on the results? "

Yes. Deriving eq. (2) we applied a linear temperature gradient (eq. (13)). A typical temperature profile in the column is characterized by a flat temperature gradient at the beginning and at the end of the tube and by a steep gradient in the center part of the column. The slope of the central gradient is linear with a regression coefficient above 0.99. To be more precise in determining the actual temperature gradient, we only considered the gradient a few centimeters in front of the peak and deduced the slope in that part of the gradient. This was done to account for the strong dependence of the partition coefficient on temperature. Partitioning to the solid phase starts to be significant only a few degrees above the deposition temperature. Furthermore, the effect of an error in the determination of the temperature gradient wouldn't strongly effect our results. The error analysis revealed that for a change in the temperature gradient of 5 K cm$^{-1}$ the adsorption enthalpy changes by 0.6 to 1.3 kJ / mol for the different nitrogen oxides.

### 4.3. "How do the authors know that the temperature gradient of an empty column is representative (i.e. within a degree or so) of one with packed spheres of ice?"

We measured the temperature at two positions inside a packed column. The temperatures were identical (within the measurement accuracy) to temperatures in an empty column. Furthermore we introduced an uncertainty of 10 K in determining the deposition temperature.

### 4.4. "How does the temperature gradient change once a gas flow begins (with warmer, upstream gas impinging on colder, downstream ice particles)? A more direct measurement of column temperature of the packed ice is needed."

Carrier gas with the flow velocity of the experiment streamed constantly through the column before the experiment was started. Only when the temperature profile in the column was stable (after 30 minutes), a small gas flow containing the $^{13}\mathrm{NO}_y$ was additionally fed to the column, without any influence on the temperature gradient.

### 4.5. "Equation 2 treats the linear gas velocity as a constant, and yet the temperature gradient must result in some variation in $\mathrm{u}_0$ across the column."

The change of the linear gas flow velocity with temperature was taken into account when deriving equation 2. See equations 14 to 16 for details.

### 4.6. "A column must be prepared of densely packed, reasonably monodisperse, well-defined spheres. Thus, the method could not be extended to liquid surfaces, and probably not mineral surfaces either."

Any material can be chosen as stationary phase, as long as the migration distance is entirely determined by the partitioning of the adsorbates between the gas- and the stationary phase. In particular liquid surfaces can not be used, as not only the adsorption equilibrium, but in addition diffusion in the liquid phase would influence the retention. In fact, this method has been used on quartz, molecular sieve, graphite, titanium oxide, vanadium oxide and several metal surfaces in open and packed columns 608, 629, 834.

The spheres in the packed column do not need to be monodisperse and well defined. Only the surface area and the open volume per column length has to be known. The measurement of the surface area by means of a BET method is even simpler with e.g. mineral dust than with ice and measuring the open volume with a flow resistance method should be possible. Note, when a BET adsorption isotherm of a material can be measured, it should be possible to do thermo-chromatography experiments with it.

## 5. BET measurements

The BET measurements, that we performed on a commercial available instrument, did not meet the quality criteria proposed by Dominé et al. (2000). Thus, we repeated BET measurements using the method proposed by Legagneux et al. (2002) with identical ice spheres to those used in our experiments. A plot of the methane adsorption isotherm of 66.3 g ice spheres, which where between 400 and 500$\mu$ m in diameter, will be included in the revised version. The BET surface area of 0.0186 m$^2$ g$^{-1}$ compares perfectly well with the geometric surface area between 0.0121 and 0.0250 m$^2$ g$^{-1}$. The geometric surface areas were calculated concidering a radius of 400 microns and a denstity of 0.6 and 500 microns and a denstity of 0.99, respectively.

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## 6. Thermodynamics: Standard States

**6.1. "I don't understand the standard state analysis, and I am not convinced that the analysis is valid. Thus, the authors are not actually measuring standard state changes; they are measuring real changes. To equate experimental measurements with a hypothetical transformation, the authors must either (i) establish that the reactant and product states do not deviate significantly from the hypothetical standard states, or (ii) correct the experimental measurements. As far as I can see, the authors did neither of those things. Rather they fit their data to eq. 2, with two assumed values of S. I am also confused by the authors' statement that both standard states yield, as expected, the same standard adsorption enthalpy. I disagree! Both H and S will depend on the choice of standard state."**

The enthalpy does simply not depend on the choice of standard state (Carmichael, 1976; Teptow, 1999). Enthalpy is defined as $\mathrm{H} = \mathrm{U} + \mathrm{p\,V}$ and the standard state of gases is defined at a certain pressure (1 bar or 1 atm). Any change in the enthalpy resulting from a change in pressure is $\Delta\mathrm{H} = \Delta\mathrm{U} + \Delta\,(\mathrm{p\,V})$. For an ideal gas at fixed temperature both U and pV are constant. Thus, $\Delta\mathrm{H} = 0$ for pressure change. In other words, the enthalpy of a gas is independent of pressure.

Thus, the standard adsorption enthalpy reflects the actual enthalpy change in our experiment and for environmental conditions (As long as it is assumed to be independent of temperature.). In other words, there is no difference between the "measured real change" and the "standard state change".

In contrast, the entropy does depend on the choice of standard state (Eq. (1)) and thus the standard adsorption entropy does not reflect the entropy change under our experimental conditions. It was, however, not the aim of our experiments to evaluate the entropy change of adsorption.

$$S = n\,R\,ln\left(e^{5/2}\frac{k_B\,T}{p}\,\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\right) \tag{1}$$

However, the use of standard states allows to determine the standard adsorption equilibrium constant. This constant does again not reflect partition under experimental (or environmental) conditions. But, using the associated standard states, it can be easily transferred to any experimental (or environmental) condition and allows comparison with equilibrium constants measured by other groups.

**6.2. "Finally, the boiling point discussion is irrelevant. the partial pressure of NO2 should be compared to the vapor pressure of NO2 at a given column temperature. Clearly, the species should be condensing near the liquid nitrogen end of the column. 3 ppbv NO2 at atmospheric pressure leads to a partial pressure of 2.3e- 6 Torr NO. In Figure 4, the peak adsorption temperature for NO2 is around 140 K. Based on extrapolated NO2 vapor pressure data from the NIST Chemistry Webbook (www.webbook.nist.gov), condensation will clearly be occurring at this temperature and partial pressure. Therefore, the NO2 results can simply be explained in terms of condensation."**

The comparison between vapor and partial pressure is as irrelevant as the boiling point discussion. We disagree to your conclusion that the partition of $NO_2$ is driven by condensation. Surface concentrations are just too low for condensation to occur during the experiments. For example, a typical experiment with 4 ppb of $NO_2$ and HONO at a flow rate of 95 ml, min$^{-1}$ yielded a surface coverage of 1 % of a formal mono layer for each nitrogen oxide at the end of an experiment. The experimental time of this run

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was 30 minutes, the surface area per centimeter in the column was 11 $cm^2$ $cm^{-1}$ and the deposition temperature was 139 K and 184 K. Peak base widths of 2 cm for the $NO_2$- and of 1 cm for the HONO peak were taken. A formal mono layer of $1 \times 10^{15}$ molecules $cm^2$ was chosen. Even at concentrations of 47 ppb $NO_y$, surface coverage did not exceed 13 % of a formal monolayer at a flow rate of 27 ml $min^{-1}$.

Under such conditions, retention is driven by the $NO_y$ - ice, rather than the $NO_y$ - $NO_y$ (ads) interaction.

### 6.3. "The best way to extract H and S from a set of data is by making measurements as a function of temperature. In the present experiment, I suppose that would involve looking at the front position for several different temperature gradients. Is such an experiment feasible?"

As the enthalpy is independent of standard state (real pressure) choice, we believe that our approach is the best way to extract the adsorption enthalpy. Our aim was not to measure the entropy change of adsorption. We rather used the entropy calculation to determine the enthalpy change. To measure the entropy change, a van‘t Hoff type plot could be used. We suggest to rather change the gas flow velocity though (Eichler et al., 1979). The temperature gradient is not easy to change experimentally, as the length of the copper tube bearing the ice column would have to be changed. Actually, we did try this approach, but it turned out, that the gas flow velocity would have to be changed in a greater extend than it is reasonable when working with packed ice columns.

### 6.4. "If not, then I don't really understand why these experiments even require the imposition of a temperature gradient. What is the advantage of this method over one in which a constant temperature is maintained throughout, and the thermodynamics of adsorption are determined through an analysis of the retention times?"

We do not have a cooling device available that allows us to maintain a constant temperature of 140K or below. Such low temperatures are necessary to measure the retention of NO and $NO_2$ on ice. The actual surface area in the column would have a much larger impact on the retention in isothermal chromatography and should thus be measured with much more care and needs to be absolutely maintained during an experiment. Each experiment would take longer. Actually it is very hard to tell when equilibrium of breakthrough curves is reached (Huthwelker et al., 2001). Additionally, as the adsorption enthalpy of nitrogen oxides are very similar, the column in isothermal chromatography should have powerful separation properties. This would require packing the ice column with ultra-small ice particles. During an experiment, a pressure gradient would build up. It might be a difficult task to control the pressure gradient and keep it stable during the course of an experiment.

P.S.:The primary observable of such an experiment would be a retention time, which could be correlated to a partition coefficient. You would still need to consider standard states just as we did in our analysis (Goss, 1997).

## 7. Acknowledgments

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