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

Anonymous Referee #1

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This manuscript describes an interesting method for measuring heats of adsorption on crystalline ice. In this method, the compound of interest is radioactively labeled and then passed over a packed column if ice spheres. A negative temperature gradient is maintained across the column, so that gas-phase molecules encounter an ever colder ice surface. At some point, the adsorbate of interest partitions irreversibly to the surface, and as a result a 'front' of immobilized molecules is formed. The position of the front, which can be determined by monitoring the radioactive decay, contains information about the thermodynamics of adsorption.

This is a very useful way of measuring the thermodynamics of NO_x and NO_y partitioning to ice. However, there are some limitations to the method which it would be worthwhile to point out. The experiments are quite difficult and they require a means of preparing radioactive versions of the adsorbates of interest. Also, a column must be

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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.

The authors provide a relatively brief derivation of the equation that relates the enthalpy and entropy of adsorption to the front position (eq. 2). Brevity is understandable given that thermochromatographic methods are well established in analytical chemistry. I was impressed that the authors carried out a sensitivity analysis of their analysis in an attempt to identify the biggest sources of systematic error. There are a few other potential sources of error that the authors may wish to consider. For example, 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.) Does eq. 2 require that the temperature gradient across the column be linear, and if not what would be the effect on the results? (The authors don't specifically state that the gradient was linear.) Eq. 2 treats the linear gas velocity as a constant, and yet the temperature gradient must result in some variation in u_0 across the column.

I don't understand the standard state analysis, and I am not convinced that the analysis is valid. The authors consider two standard states for the adsorbed state, both of them hypothetical. (As the authors point out, the choice of standard state is arbitrary, although some choices are more useful than others.) 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 ΔS°. I am also confused by the authors' statement that both standard states 'yield, as expected, the same standard adsorption enthalpy.' I disagree! Both ΔH° and ΔS° will depend on the choice of standard state. Moreover, the authors ought to be able to estimate the enthalpy difference between the two standard states, just as they estimated values for the entropy change upon adsorption. Did they do so, and have they shown that the difference is smaller than experimental error? I'd be surprised if that were the case: the $\exp(\Delta S^\circ/R)$ term in eq. 2 changes by 6 orders of magnitude when ΔS° is changed from -44 to -168 J mol^{-1} K^{-1}. Shouldn't there be a reasonably large corresponding change in ΔH°?

The best way to extract ΔH and ΔS 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? 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? There are numerous misspellings and unclear passages, e.g.:

1. Replace 'gas phase' by 'gas-phase' on line 10 of p 433.

2. I don't understand the first paragraph of the Experimental section. How can NO be formed from the reaction of a proton beam with ^{13}N?

3. Synthesis is misspelled on line 22 of page 435.

4. On line 8 of page 436: Why was the ice density assumed as 0.8 g cm^{-3}?

5. In the BET section (pages 436 and 437): If the surface area of an ice 'chunk' was 'negligible,' why was it necessary to 'subtract' the isotherm? What exactly do the authors mean by subtracting an isotherm anyway?

6. Waterloo Maple should be capitalized on line 4 of page 439.

7. The argument about condensation in the first paragraph of the Results and discussion section is misleading. The boiling point of a substance corresponds to the

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temperature at which the vapor pressure is 1 atm. In order to establish that the observed process is adsorption and not condensation, the authors must compare the deposition temperature to the condensation temperature at the relevant NO_x pressure.

8. The meaning of the paragraph following eqs. 5 and 6 is unclear.

9. 'Gibbs' should be capitalized in line 12 of page 448.

Interactive comment on Atmos. Chem. Phys. Discuss., 2, 431, 2002.