**Atmospheric
Chemistry
and Physics
Discussions**

Interactive
Comment

Interactive comment on "The uptake of SO$_2$ on Saharan dust: a flow tube study" *by* J. W. Adams et al.
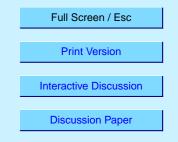
J. W. Adams et al.

Received and published: 5 August 2005

The following are replies to the **Comments of referee 1**

General Comments:

Comment 1: The use of the total (external and internal) surface area A(BET) in the evaluation of the initial uptake coefficient gamma0,BET implies that the probe gas, SO$_2$, explores the total surface area within the contact time of 50-100 ms, thereby giving rise to the maximum rate of uptake observed at t = 0 when the injector is pushed back, unless I misunderstand. Naturally, the modeled rate of adsorption results in the same situation as the rate constant kads has been chosen accordingly. I would like to raise the question whether this is reasonable. Taking as an example the measurement of

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

EGU

BET isotherms of nitrogen on Al_2O_3 of comparable BET surface area as Saharan dust one invariably observes a pressure relaxation period of 9 to 12 minutes after every new addition of nitrogen starting at a fraction of a mbar up to one atmosphere of nitrogen. During this time the pressure drops continuously because N_2 is undergoing pore diffusion until equilibration is reached. This seems to be in conflict to the assumption made by the authors on the bottom of pg. 2649 ("If we assume the SO_2 gas can access the whole of the BET surface area instantly, then [...]"). The question here is one of time scale of pore diffusion. - In order to solve this dilemma I would encourage the authors to emphasize that the initial uptake coefficient gamma0,BET is certainly a lower limit to the "true" uptake coefficient. In this case one cannot speak of the "true" value. In uptake experiments of HNO_3 on mineral dust aerosol one observes that the resulting uptake coefficient is much closer to gamma0,geom than to gamma0,BET.

Reply: We are in agreement with the referee. The use of the BET surface area to calculate a gamma will result in a lower limit, as not all of the surface is instantly available to the SO_2 gas. The BET surface area is used to allow comparison with uptake coefficients reported in the literature. The paragraph where gamma BET is defined has been reworded and a line added indicating that gamma BET is a lower limit to the 'true' gamma.

Comment 2: When talking about "unhumidified" Saharan dust could the authors give an indication of the amount of adsorbed water?

Reply: The amount of water remaining on an unhumidified dust sample is unknown. However, the surface preparation method used will remove the majority of weakly bound water molecules.

Comment 3: An alternative, potentially more instructive way of describing the amount of adsorbed SO_2 molecules (pg. 2654) would be to evaluate this quantity at an equal

number of collisions with the dust substrate as a function of initial partial pressure of SO_2 rather than upon integration over 200s which seems a bit arbitrary.

Reply: The choice of the cumulative SO_2 adsorption after 200 s is indeed arbitrary, but it allows (i) most of the experimental runs to be used (ii) a comparison between the amount of strongly adsorbed SO_2 and the amount desorbed when exposure ceases, and (iii) comparison between experimental data and model predictions.

Comment 4: The data plotted in Figure 7 at low initial SO_2 concentration do not appear to lie on a straight line with the data at higher concentration. I understand the reasons for wanting to preserve the simple Langmuir adsorption model discussed on page 2657, however, allowance should be made for curvature potentially owing to mechanistic complications at low SO_2 initial concentration which is of atmospheric relevance.

Reply: The fit of the Langmuir isotherm is reasonable given the scatter in the data. If there were to be mechanistic complications they would be expected to be more significant at higher rather than lower initial SO_2 concentrations.

Comment 5: Concerning the "presence of ozone on the mineral dust surface" (pg. 2657, line14): do the authors have proof that ozone is in fact adsorbed on dust and may therefore partake in a Langmuir-Hinshelwood mechanism, or is it simply O_3 and SO_2 co-flowing? On pg. 2655, line 15, the authors talk about the "presence" of O_3 which I understand as a co-flow experiment.

Reply: Although we have no direct probe of the dust surface other groups have seen evidence of surface bound ozone on metal oxides. A summary of this evidence is given in Usher *et al.* (2003). The paper text has been changed to reflect that we are assuming ozone is bound to the surface.

Comment 6: If one calculates the rate of adsorption (R1), namely, rate = kads (SO$_2$), where (SO$_2$) is the SO$_2$ concentration given in molecule cm(-3) using the expression for kads given in equation (4), I end up with unphysical units of cm(-1)s(-1) for a chemical rate. Instead, it should be either molecule s(-1) or molecule cm(-3)s(-1) (pg. 2660). Please explain!

Reply: The wrong units were used for S$_0$ (should have been molecule cm^{-3}). This error has been corrected and the units for the rate of R1 are now a more physical molecule cm^{-3}s^{-1}. In addition some of the values reported in table 2 were given in surface densities, rather than volume densities. These units have now been corrected. An extra sentence has also been added to the paper explaining that: "Here all concentrations (including surface site concentrations) are in units of molecule cm^{-3}, i.e. number density per unit volume of the flow tube."

Comment 7: What is the physical basis of using equation (6) (Pg. 2660) for the kinetics of pore diffusion? This expression is borrowed from solubility-limited uptake of trace gases into fluid media implying a t(-0.5) dependence. Has such a dependence been observed for pore diffusion before? If yes, please provide the proper reference.

Reply: Pore diffusion in the model has been approximated using an expression for diffusion into a bulk film. The expression comes from the solution of the diffusion equation for Fick's Law with a specified mean diffusion depth L and gives an expression for the time dependence of the rate coefficient for diffusion of surface adsorbed species into the bulk. Sorption kinetics models, described in the literature (e.g. Ran et al Environ. Sci. Technol. 2005), use time dependent expressions derived from a solution of the diffusion equation. The text of the paper has been clarified.

Comment 8: I understand that the parameter (D(L))(0.5)/L has been used as an adjustable parameter. What is a typical value for D(L) at a reasonable choice of L? Is it

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

EGU

compatible with free molecular flow (Knudsen diffusion) inside the pores as one would expect? This question is related to the point made above.

Reply: As the use of this expression is an approximation to pore diffusion it is difficult extract anything meaningful from the separation of the two parameters D and L. However, for the diffusion of benzene into a zeolite (a diffusion controlled process), Beschmann *et al.* in *Characterization of Porous Solids*, Ed. Unger *et al.*, Elsevier Science Publishers, The Netherlands, 1988) reported a value of D/L^2 of 0.041 s^{-1}. For comparison, the current work gives a value of 0.15 s^{-1}.

EGU