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Atmospheric
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Discussions

Interactive comment on “Influence of the ice growth rate on the incorporation of gaseous HCl” *by* F. Domine and C. Rauzy

Anonymous Referee #3

Received and published: 6 October 2004

General Comment:

The paper by Domine and Rauzy (DR) presents and discusses results of a careful experimental study which investigates the fraction of HCl incorporated in ice growing at different rates. The ice growth rate is controlled by different ice supersaturations maintained by different water content of a constant air flow cooled to a temperature of $-15°C$ inside a so-called crystallization tube. The HCl concentration was kept constant during all experiments. The experimental results are compared to a model published by Domine and Thibert (1996). This model distinguishes between fast growth rates with kinetic control of HCl uptake and slow growth rates with HCl uptake close to thermodynamic equilibrium. In my view, the paper addresses important issues of gas uptake to ice and is worth a discussion paper. For publication as a full ACP paper, however, I recommend some revision and improvement as specified below.

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Specific comments and questions:

On page 4724, line 17, DR state that X_{kin} “tends asymptotically towards a value around 10 ppb". The major result and conclusion of the present paper rely on this statement which is very critical regarding the following aspects:

(1) According to equation (1) I would expect X_{kin} to be proportional to $1/p_{H2O}$ and thus to $1/(1+supersaturation/100)$ provided that p_{HCl} and the accommodation coefficients are constant;

(2) It is very difficult to conclude a trend from a plot of only 3 points, especially because there is only one experiment at 40% supersaturation. Considering the uncertainty of this data point and also of the supersaturation (see below) the points may follow even a straight line.

Furthermore, there seem to be a problem with calculating the ratio $\alpha_{HCl}/\alpha_{H2O}$. At $-15°C$, the ice saturation pressure $pw_{ice} = 166$ Pa. At 82.5 $\%$ supersaturation with $X_{HCL} = 11$ ppb and $p_{HCl} = 0.00167$ Pa I get $\alpha_{HCl}/\alpha_{H2O} = 11 \cdot 10^{-9} \cdot 166 \cdot 1.825/0.00167/\sqrt{18/35} = 0.0028$. At 40 $\%$ and 15 $\%$ supersaturation one gets values of 0.0047 and 0.025, respectively, with X_{HCL} given in table 1. Because even at the lowest ice growth rate at 15 $\%$ supersaturation the measured X_{HCL} is much smaller than the respective equilibrium value as mentioned on page 4724, line 12, I suggest to discuss the ratio of accommodation coefficient within the range of all experiments. Any discussion of trends or non-kinetic contributions to the results is, in my view, rather speculative on the basis of the presented results. I also suggest adding, instead of the arbitrary line in Fig. 1, a fit of X_{HCL} according to equation (1), either with a mean value or a possible range of $\alpha_{HCl}/\alpha_{H2O}$ to explain the experimental results.

Further experiments at intermediate supersaturations and probably also other temperatures would give much more confidence on the most important conclusions of the paper.

I agree with referee 1 that the description of the experiments and methods is insufficient. The following points and questions need to be addressed:

Was the temperature of the upstream bubbler and therefore the water content of the gas mixture controlled properly?

Was the water content measured independently upstream and downstream of the crystallization tube ?

Did the temperature of the gas mixture cool below the frost point temperature before leaving the glass sphere, especially during the experiments at high supersaturations, or in other words, was there any ice deposition in the glass sphere that could affect the water mass balance and the supersaturation in the crystallization tube?

On page 4723, line 16, DR mention that most of the water in excess of ice saturation at $-15^{\circ}C$ deposited to the ice phase. That implies a strong gradient of ice supersaturation along the ice deposition region. The results, however, are presented only in terms of the maximum ice supersaturation calculated, probably, from the water content of the warm mixture and the saturation pressure at $-15^{\circ}C$. If possible, the uncertainty range of ice saturation (and also temperature) during ice deposition must be specified or at least estimated. Was this uncertainty e.g. checked by scraping and analyzing ice from different deposition regions in the crystallization tube?

Non-uniform ice deposition conditions also add significant uncertainty to the discussion of the ice growth steps. This should also be considered and mentioned explicitly.

DR briefly mentioned that the measured X_{HCL} have been corrected for blank values. The amounts and scatter of these values should explicitly be mentioned.

Minor comments:

p.4723, l.2: . . . were flown into

p.4723, l.20: Numerous tests and blanks . . . Which ones?

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p.4724, l.16: . . . at three pH2O values, . . . (you may also add p_{H2O} to table 1).

p.4725, l.20 to 26: I missed the point here. What means e.g. "$\ldots\alpha_{HCL}$ could be affected by the same variables . . . , and possibly in a different way."'? Please clarify.

p.4725, l.29: . . . could merely reflect the . . .

p.4727, l.17: . . . growth steps, which suggests that . . .

p.4729, l.2: . . . be more concentrated in Cl^- than the . . .

p.4729, l.11: . . . the data available suggests that . . .

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 4719, 2004.

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