

## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet V.A4.3 HSTD3

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This data sheet last evaluated: January 2009; last change in preferred values: January 2009.

### HCl + SAT

#### Experimental data

Parameter	Temp./K	Reference	Technique/ Comments
<i>Partition Coefficient: <math>K_{inc}</math> (<math>\text{cm}^2 / \text{cm}^3</math>)</i>			
6800 (RH = 79.4 %)	195 K	Zhang et al., 1994	FT-MS (a)

#### Comments

- (a) Sulphuric acid tetrahydrate films (> 0.1 mm thick) were generated by freezing H<sub>2</sub>SO<sub>4</sub> solutions (57.7 wt %) at 200 K. The relative humidity above the film was varied by adjusting the temperature at fixed H<sub>2</sub>O partial pressure or by adjusting the H<sub>2</sub>O partial pressure at fixed temperature to form either H<sub>2</sub>O-rich or H<sub>2</sub>SO<sub>4</sub>-rich forms of SAT. The geometric surface area was used to calculate the uptake coefficient.

#### Preferred Values

Parameter	Value	T/K
$K_{inc} / \text{cm}$ (RH = 79.4 %)	6800	195
$F$	$\frac{-2.47 \times 10^{11} + 3.28 \times 10^{11} \cdot RH + 3.27 \times 10^9 \cdot RH^2 + 2.43 \times 10^8 \cdot RH^3}{1.7 \times 10^{14}}$	
<i>Reliability</i> $\Delta \log N$	0.5	190 - 199 K

#### Comments on Preferred Value

The interaction of HCl with sulphuric acid tetrahydrate film shows a strong dependence on both temperature and the pressure of water vapour, with the H<sub>2</sub>O-rich form of SAT accommodating more HCl at the surface than the H<sub>2</sub>SO<sub>4</sub>-rich form. Zhang et al. (1994) present three separate parameterisations of the HCl surface coverage ( $N$ ) with either  $T$ ,  $p_{\text{H}_2\text{O}}$  or  $p_{\text{HCl}}$  as variables. The value of  $K_{inc}$  listed in the Table was taken from a dataset in which  $p_{\text{HCl}}$  was systematically varied at a fixed temperature and fixed  $p_{\text{H}_2\text{O}}$ . Only data taken at low  $p_{\text{HCl}}$  ( $p_{\text{HCl}} < 2 \times 10^{-6}$  Torr) were considered as here the adsorption isotherm is approximately linear and this range of pressures is relevant for the atmosphere.

The dependence of surface coverage ( $N$ ) on temperature is very large, with a change < 10K resulting in a factor of 100 change in  $N$  indicating that the surface interaction is driven by the availability of H<sub>2</sub>O. We have taken the observed dependence of the surface coverage on  $p_{\text{H}_2\text{O}}$  at a fixed temperature to derive the dependence of  $N$  on the relative humidity (relative to pure ice

as given in Marti and Mauersberger, 1995) and provide a parameterisation for the surface coverage ( $N$ ) that requires only the relative humidity and the HCl concentration as input.

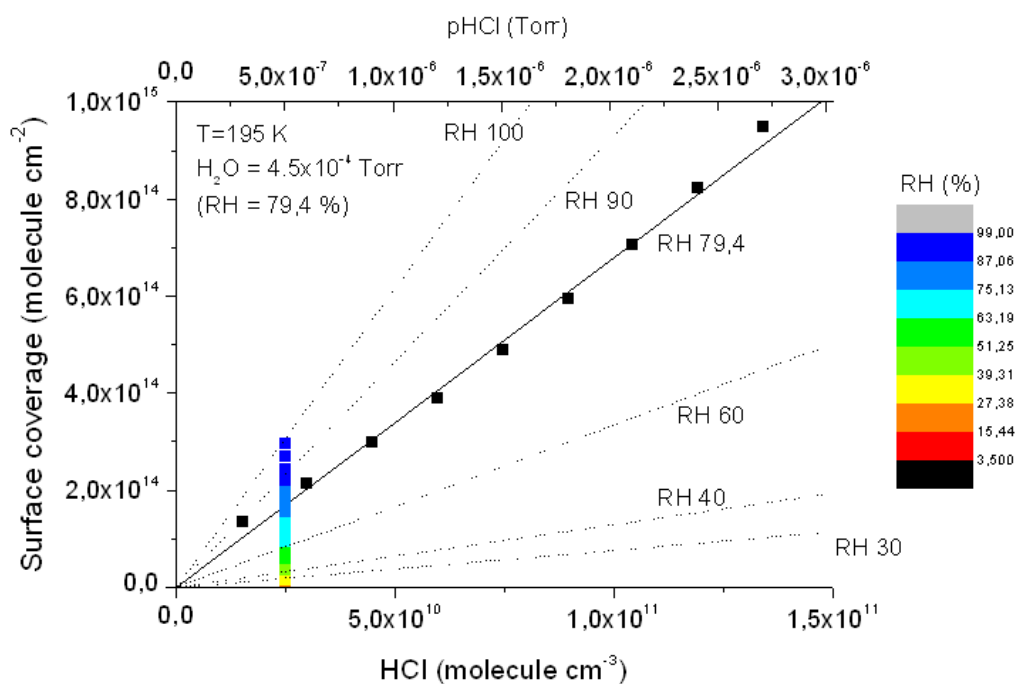
$$N = 6800[\text{HCl}] F, \text{ where } [\text{HCl}] \text{ is in molecule cm}^{-3} \text{ and RH is given by } 100 P_{\text{H}_2\text{O}} / P_{\text{ice}}$$

Note that the parameterisation assumes that the low partial pressure HCl isotherm is linear at all relative humidities and is probably not valid for high partial pressures of HCl (e.g. greater than  $10^{-6}$  Torr). It does however reproduce the data of Zhang et al. (1994) between to within a factor of two for  $T < 200$  K.

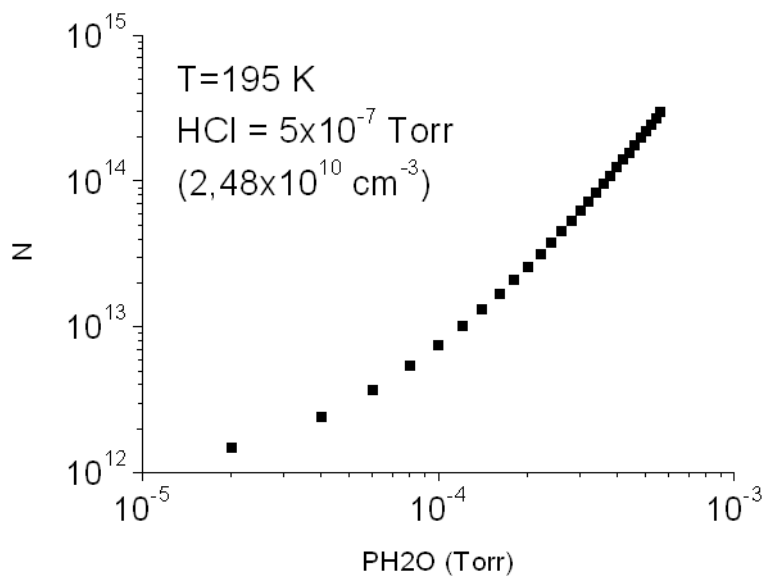
### References

Marti, J. and Mauersberger, K.: Geophys. Res. Lett. 20, 363-366, 1993.

Zhang, R. Y., Jayne, J. T. and Molina, M. J.: J. Phys. Chem. 98, 867-874, 1994.



Surface coverage of HCl on SAT. The datapoints measured at a  $RH$  of 79.4 % ( $T = 195$  K,  $p_{\text{H}_2\text{O}} = 4.5 \times 10^{-4}$  Torr) are from the expression given by Zhang et al., 1994. The solid / dotted lines are taken from the parameterisation given above. The colour coded dataset was taken from the parameterisation given by Zhang et al. for a dataset obtained by variation of  $p_{\text{H}_2\text{O}}$  at fixed  $p_{\text{HCl}}$  and at 195 K.



HCl + SAT- Dependence of N on the partial pressure of H<sub>2</sub>O (taken directly from the parameterisation given by Zhang et al., 1994).