

## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet V.A1.27 HI27

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### HCl + ice

#### Experimental data

Parameter	Temp./K	Reference	Technique/ Comments
<i>Experimental uptake coefficients: <math>\gamma</math>, <math>\gamma_0</math></i>			
$\gamma_0 > 0.2$	197	Leu, 1988	CWFT-MS (a)
$\gamma_{ss} = (4.0 \pm 2.0) \times 10^{-4}$	196	Leu, Moore and Keyser, 1991	CWFT-MS (b)
$\gamma_{ss} > 0.2$	191 - 200	Hanson and Ravishankara, 1992	CWFT-MS (c)
$\gamma_{ss} > 0.2$	188 - 193	Chu, Leu and Keyser, 1993	CWFT-MS (d)
$0.34 \pm 0.03$	190	Flückiger et al, 1998	Knudsen-MS (e)
$0.26 \pm 0.02$	200		
$0.22 \pm 0.02$	210		
$\gamma = (7 \pm 3) \times 10^{-2}$	205	Hynes, Mössinger and Cox, 2001	CWFT-MS (f)
$(1 \pm 0.3) \times 10^{-2}$	215		
$(5 \pm 2) \times 10^{-3}$	230		
<i>Partition coefficients: <math>K_{LinC}</math> (cm)</i>			
$3.8 \times 10^{-4}$	190	Huthwelker et al., 2004	Knudsen-MS (g)
48.5	203		
$(5.4 \pm 0.3) \times 10^4$	208	Fernandez, Hynes and Cox, 2005	CWFT-MS (h)
$(1.68 \pm 0.12) \times 10^4$	218		
$(0.78 \pm 0.6) \times 10^4$	228		
$1.20 \times 10^4$	196	McNeill et al, 2007	CWFT-MS (i)
$2.19 \times 10^4$	203		
$1.89 \times 10^3$	213		
$8.02 \times 10^3$ ( $11.9 \times 10^3$ )	190	Zimmermann et al., 2016	CWFT-CIMS (j)
$7.24 \times 10^3$ ( $25.8 \times 10^3$ )	200		
$6.14 \times 10^3$ ( $23.9 \times 10^3$ )	210		
$8.40 \times 10^3$ ( $30.8 \times 10^3$ )	220		

#### Comments

- Ice condensed from the vapour phase. The amount of HCl taken up by ice increased with  $p_{\text{HCl}}$  and decreasing temperature, and with ice thickness.
- Ice was condensed from the vapour phase.
- Ice was condensed from the vapour phase at 196 K. The data were corrected for pore diffusion using a two-site surface reaction model;  $p_{\text{HCl}} \sim 10^{-2}$  mbar to  $10^{-4}$  mbar.

- (d) Vapour deposited ice. For  $[\text{HCl}] \sim 10^{10}$  molecule  $\text{cm}^{-3}$   $\gamma$  was time dependent due to surface saturation, for  $[\text{HCl}] \sim 2 \times 10^{12}$  molecule  $\text{cm}^{-3}$   $\gamma (> 0.3)$  was time independent due to formation of a new phase.
- (e) Vapour deposited ice. Pulsed valve and steady-state experiments were performed with  $p_{\text{HCl}}$   $6.7 \times 10^{-7}$  mbar to  $2.7 \times 10^{-4}$  mbar.  $\gamma$  values reported were obtained under conditions where a quasi-liquid layer of HCl-H<sub>2</sub>O on the surface was present.
- (f) Ice made by freezing liquid water. The calculated coverage of HCl on ice is only weakly dependent on temperature and  $P_{\text{HCl}}$  in the range  $(0.5 - 2.7) \times 10^{-6}$  mbar. It leads to an average saturation coverage of HCl on ice of  $(2.0 \pm 0.7) \times 10^{14}$  molecules  $\text{cm}^{-2}$  at 205K using the geometric surface area.
- (g) Vapour deposited ice. HCl partial pressure range  $4 \times 10^{-8}$  to  $2.3 \times 10^{-5}$  mbar.  $N$  was separated into a non-diffusive and a diffusive component, which displayed a  $t^{0.5}$  dependence and was proportional to  $p_{\text{HCl}}^{-0.5}$ . Values for  $K_{\text{Lang}}$  were derived from parametrization of  $N$  and its dependence on exposure time, temperature, HCl acidity constant on ice, Henry's law constant for physical solubility of HCl and the diffusion constant of HCl in the diffusion layer.
- (h) Co-adsorption of HCl and HNO<sub>3</sub> ( $1.0 \times 10^{-6}$  Torr) on frozen film ice at 208 - 228K. Partition coefficients cited were determined using the non-dissociative Langmuir expression, using partition coefficients for HNO<sub>3</sub> fixed at the values given in Cox et al (2005).
- (i) Zone-refined, vapour deposited ice using ellipsometry to monitor ice surface and CIMS detection of gas uptake. At the centre of the ice stability region the uptake is reversible. HCl coverages were analysed with the non-dissociative Langmuir expression.
- (j) Ice made by freezing liquid water. The dissociative Langmuir isotherm was observed to best describe the data and the partition coefficient listed first in the Table were derived this way. The partition coefficients in brackets were derived using the non-dissociative Langmuir isotherm.

### Preferred Values

Parameter	Value	T/K
$\alpha_s$	0.3	190 - 210
$N_{\text{max}} / \text{molecule cm}^{-2}$	$2 \times 10^{14}$	190 - 230
$K_{\text{LinC}} / \text{cm}$	19200	190 - 230
<i>Reliability</i>		
$\Delta \log (\alpha_s)$	$\pm 0.3$	190 - 210
$\Delta \log (K_{\text{LinC}}) / \text{cm}$	$\pm 0.3$	205 - 230
$\Delta \log (N_{\text{max}}) / \text{molecule cm}^{-2}$	$\pm 0.2$	

### Comments on Preferred Values

There have been many experimental studies on the HCl – ice interaction. Most earlier studies were at temperatures  $< 200$  K and concentrations corresponding to stability regions of the phase diagram for either hydrate or supercooled HCl/H<sub>2</sub>O solutions. Under these conditions uptake is continuous and irreversible. In the ‘ice stability’ region, the experimental uptake coefficient is time dependent, declining from an initial rapid uptake ( $\gamma \sim 0.1$ ) to very slow uptake when the surface saturates. Pulsed Knudsen cell measurements of  $\gamma_0$  (Flückiger et al., 1998) indicate that the surface accommodation coefficient ( $\alpha_s$ ) is  $>0.3$  at temperatures below 200 K.

In some experiments, either  $\gamma$  or the integrated surface coverage ( $N$ ) can be divided into rapid and slow components. The slow component has been shown to be diffusive in character

(Huthwelker et al, 2004; Cox et al, 2005) and to increase in rate near the boundary of the ice stability region. Ellipsometric observations of ice films exposed to HCl (McNeil et al, 2006) show that surface melting to form a quasi-liquid layer up to 100nm thick results from adsorption of HCl in this region, which is consistent with the observed uptake behaviour.

In the ice-stability regime, HCl adsorption is partially reversible and has been described using a Langmuir model. HCl surface coverages on ice films in the temperature range 200-240 K have been reported in several studies (Abbatt, 1992; Hanson and Ravishankara, 1992, Chu et al., 1993, Abbatt, 1997; Barone et al., 1999, Lee et al, 1999; Hynes et al., 2001, Hynes et al., 1999 and 2002; Sokolov and Abbatt, 2002; Huthwelker et al, 2004; Fernandez et al., 2005). The surface coverage at saturation,  $N_{max}$ , is between  $1-3 \times 10^{14}$  molecule  $cm^{-2}$ , for smooth ice surfaces, i.e. those formed by freezing liquid water or by zone refining vapour deposited ice (Hynes et al. 2001; and Lee et al., 1999; McNeill et al., 2007; Zimmermann et al., 2016) and are thus consistent with values for other trace gases on similar ice surfaces, and with molecular dynamics calculations (Abbatt, 2003). Our preferred value for  $N_{max}$  is taken from the studies on smooth ice of Hynes et al. (2001), McNeill et al. (2007) and Zimmermann et al. (2016).

Several studies report a weak dependence of  $N$  on  $p_{HCl}$ , but only three (Huthwelker et al., 2004; McNeill et al., 2007; Zimmermann et al., 2016) investigated the  $p_{HCl}$  dependence of surface coverage in the unsaturated region of the Langmuir isotherm on a pure ice surface and were thus able to derive Langmuir partition coefficients. McNeill et al. concluded that their data were best described by the non-dissociative form of the Langmuir isotherm, whereas Huthwelker et al (2005) and Zimmermann et al., (2016) prefer the dissociative form. This may be related to the different modes of ice film generation used. As the uptake of HCl to the vapour deposited ice of Huthwelker et al. (2004) was dominated by slow, diffusive uptake into the bulk of the ice film, we consider only the low coverage data of McNeill et al (2007) and Zimmermann et al (2016) for the preferred values of the Langmuir partition coefficients ( $K_{Lang}$ ). Both studies report no monotonic dependence of ( $K_{Lang}$ ) on temperature so that we take a temperature independent, unweighted, average value from these studies. Note that in order to combine datasets, we have taken the non-dissociative Langmuir constants and associated values of  $N_{max}$  reported by both groups to derive the temperature independent value of  $K_{linC}$  reported above.

For the purpose of calculating the surface coverage ( $N$ ) of HCl on atmospheric ice surfaces the values of  $K_{linC}$  tabulated above should be used in conjunction with the non-dissociative form of the Langmuir isotherm.

$$\frac{N}{N_{max}} = \frac{K_{LangC}[HCl]}{K_{LangC}[HCl]+1} \quad \text{where } K_{LangC} = K_{linC} / N_{max}$$

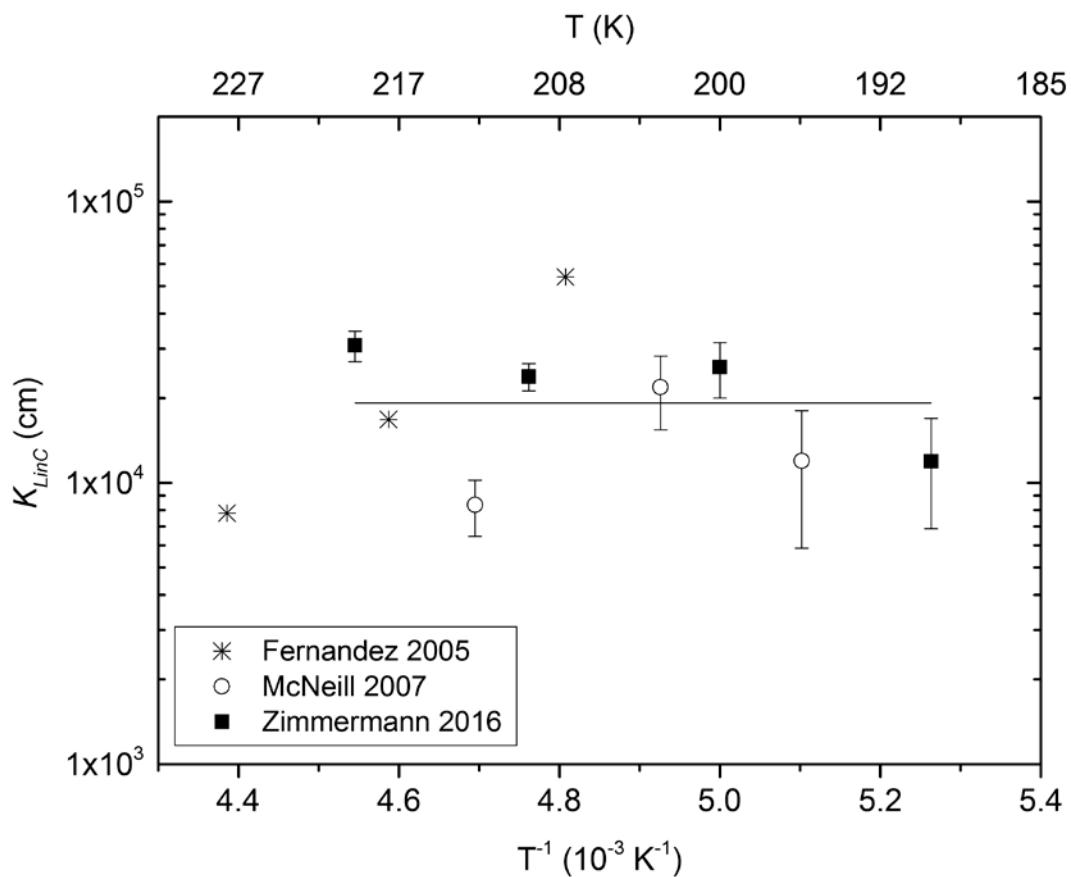
We note that Fernandez et al. (2005) report reduced HCl coverages on ice surfaces that are simultaneously exposed to  $HNO_3$ , a result of competitive adsorption. Extracting the Langmuir partition coefficient for HCl from this dataset requires detailed knowledge of the  $HNO_3$  isotherm, which is however associated with great uncertainty.

Several studies report a non-reversible component to the uptake of HCl to fresh ice with the amount of HCl observed to desorb significantly lower than that adsorbed. (Hanson and Ravishankara, 1992; Hynes et al., 2001; McNeill et al., 2007; Flückiger et al., 2000; Zimmermann et al., 2016). This is probably related to the facile ionisation of HCl on ice which has been demonstrated both experimentally (Graham and Roberts, 1994; Devlin et al. 2002; Buch et al., 2002; Park et al., 2005; Ayotte et al., 2011; Parent et al., 2011; Riikonen et al., 2014) and theoretically (Clary and Wang, 1997; Svanberg et al., 2000; Bolton and Pettersson, 2001; Bolton 2003; Gerber et al., 2015). The apparently non-reversible component of uptake is somewhat variable from one experiment to the next and can exceed the reversible component by factors of 1.5 to 2.5 (Hynes et al., 2001; Hanson and Ravishankara, 1992; McNeill et al., 2007;

Flückiger et al., 2000). This is not considered in the parameterisation using the Langmuir isotherm.

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**HCl partitioning to ice.** Values of  $K_{Linc}$  were taken from experimental studies in which the non-saturated part of the HCl-ice isotherm was investigated. The solid line is the temperature independent IUPAC preferred value of  $K_{linC} = 19200$ .