

# IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet V.A1.20 HI20

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## Methanol + ice

### Experimental data

Parameter	Temp./K	Reference	Technique/ Comments
<i>Experimental uptake coefficients: <math>\gamma</math>, <math>\gamma_0</math></i>			
$\gamma_0 > 0.02$	198	Winkler et al., 2002	CWFT-MS (a)
$\gamma_0 > 0.1$	150-160	Hudson et al., 2002	Knudsen (b)
$\gamma_0 > 0.04$	170		
<i>Partitioning coefficients: <math>K_{inc}</math></i>			
$K_{inc} = 6.24 \times 10^{-12} \exp(6178/T)$	198-223	Winkler et al., 2002	CWFT-MS (c)
$K_{inc} = 3.82 \times 10^{-10} \exp(4980/T)$	140-170	Hudson et al., 2002	Knudsen (d)

### Comments

- (a) 50-100  $\mu\text{m}$  thick ice film (geometric area  $\approx 100 \text{ cm}^2$ ) made by freezing water.  $\gamma_0$  (calculated from the geometric ice surface area) is a lower limit as adsorption and desorption were not separated in time.
- (b) vapour deposited ice film of geometric area  $\approx 5 \text{ cm}^2$ .  $\gamma_0$  values taken from a Figure.  $\gamma_0$  is a lower limit as adsorption and desorption were not separated in time.
- (c)  $K_{inc}$  determined from linear relationship between  $N$  (surface coverage in molecule  $\text{cm}^{-2}$  of ice) and [methanol] (units of molecule  $\text{cm}^{-3}$ ) at low coverage where  $N < 1 \times 10^{13} \text{ molecule cm}^{-2}$  ( $K = N / [\text{methanol}]$ ). The geometric surface area was used to calculate the coverage. Analysis of datasets including measurements at higher coverage using a Langmuir isotherm, resulted in lower values of the partitioning coefficient, potentially a result of adsorbate-adsorbate interactions.  $N_{\text{max}} = (3.2 \pm 1.0) \times 10^{14} \text{ cm}^{-2}$ . Enthalpy of adsorption derived as  $\Delta H_{\text{ads}} = (-51 \pm 10) \text{ kJ mol}^{-1}$ .
- (d) The geometric surface area of the vapour deposited ice film was used to calculate the coverage. Equilibrium uptake of methanol ( $\approx 10^{10} \text{ molecule cm}^{-3}$ ) to ice at various temperatures was analysed using the Langmuir isotherm, with  $N_{\text{max}}$  assumed to be  $4 \times 10^{14} \text{ molecules cm}^{-2}$ . The expression given in the Table uses the reported values of  $\Delta S_{\text{ads}}$  (via Trouton's rule) of  $-87.9 \text{ Jmol}^{-1} \text{ K}^{-1}$  and an experimental value of  $\Delta H_{\text{ads}} = -41.4 \text{ kJmol}^{-1}$ .

### Preferred Values

$K_{inc} = 6.24 \times 10^{-12} \exp(6180/T) \text{ cm}$  over the range 195 K to 230 K.  
 $N_{\text{max}} = 3.2 \times 10^{14} \text{ molecules cm}^{-2}$ , independent of temperature.

## Reliability

$$\Delta(E/R) = \pm 100 \text{ K.}$$

$$\Delta \log N_{\max} = 0.15$$

## Comments on Preferred Values

The two experimental studies of the methanol – ice interaction show that, at low methanol concentrations, the adsorption of acetone to ice is completely reversible. The data of Winkler et al. (2002) show significantly higher coverage at 200 K than those calculated from the parameterisation of Hudson et al. (2002), who were unable to observe methanol adsorption at this temperature. Bearing in mind that the same experiments of Hudson et al. (2002) provided the only outliers in several datasets measuring acetone adsorption to ice, the data of Winkler et al. are preferred, and form the basis of the recommendation. Equilibrium surface coverages at higher concentrations can be calculated using the full form of the Langmuir isotherm (Winkler et al., 2002). No evidence was found for enhanced uptake or product formation when films containing 1 monolayer of HNO<sub>3</sub> (Hudson et al., 2002) or films which were in equilibrium with  $\approx 10^{12}$  molecule cm<sup>-3</sup> of gas phase O<sub>3</sub> at 198 K (Winkler et al., 2002).

Measurements of the experimental uptake coefficient are problematic due to the simultaneous desorption of methanol from the surface, which, apart from at the lowest temperatures, will result in determination of a lower limit. No recommendation is given for  $\gamma$  or S<sub>0</sub>.

Theoretical investigations (Picaud et al, 2000; Collignon and Picaud, 2004) suggest that the OH group of methanol is associated with the ice surface and predict a maximum coverage of  $\approx 4 \times 10^{14}$  molecule cm<sup>-2</sup> at 210 K, consistent with the observations. At low surface coverages, methanol is bound to either one or two H<sub>2</sub>O molecules, whereas at high surface coverages, adsorbate-adsorbate interactions become important such that the Langmuir analysis breaks down and the N<sub>max</sub> is difficult to access (Jedlovszky et al., 2006).

## References

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Picaud, S., Toubin, C. and Girardet, C.: Surface Science 454, 178-182, 2000.  
Winkler, A. K., Holmes, N. S. and Crowley, J. N.: Phys. Chem. Chem. Phys. 4, 5270-5275, 2002.