

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet VIA4.14 HET_SL_14

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HCl + H₂SO₄ (aqueous) → products

Experimental data

<i>Parameter</i>	[H ₂ SO ₄] /wt %	Temp./K	Reference	Technique/ Comments
<i>Uptake coefficients: γ</i>				
$\gamma_{ss} = 1.5 \times 10^{-3}$	65	210	Tolbert et al., 1988	Kn-MS (a)
$\gamma_{ss} = 2.6 \times 10^{-4}$	70	220		
$\gamma_{ss} > 8.5 \times 10^{-5}$	70	230		
$\gamma = (1.5 \pm 0.2) \times 10^{-1}$	20	283	Watson et al., 1990	DT-TDLAS (b)
$\gamma = (1.6 \pm 0.3) \times 10^{-1}$	35			
$\gamma = (1.5 \pm 0.2) \times 10^{-1}$	40			
$\gamma = (1.0 \pm 0.1) \times 10^{-1}$	47			
$\gamma = (7.9 \pm 0.6) \times 10^{-2}$	52			
$\gamma = (4 \pm 6) \times 10^{-3}$	58			
$\gamma = (0 \pm 4) \times 10^{-3}$	73			
<i>Accommodation coefficients: α_b</i>				
0.8 ± 0.2 (HOCl doped)	34	274	Hanson and Lovejoy, 1996	RWFT-CIMS (c)
1.1 ± 0.1	39	230	Robinson et al., 1998	DT-TDLAS (d)
0.93 ± 0.07	39	240		
0.75 ± 0.06	39	252		
0.65 ± 0.06	39	261		
0.95 ± 0.08	49	233		
0.90 ± 0.08	49	244		
0.80 ± 0.11	49	254		
0.53 ± 0.07	49	261		
10 ⁻²	30-40	185-207	Schwell et al., 2000	EDB (e)
$\alpha_s > 0.9$	70	213	Morris et al., 2000	MB (f)
$\alpha_b \approx 0.1$	70			
0.75	53	213	Behr et al., 2001	MB (g)
0.52	60			
0.27	65			
0.12	69			
0.1	70.5			
0.66	58	213	Behr et al., 2009	MB (h)
0.50	63			
0.28	67			
0.25	74			
0.33	72	213		
0.38	72	218		
0.42	72	223		
0.44	72	233		

0.47	72	238		
<i>Solubility: H ($M atm^{-1}$); Diffusion: D_1 ($cm^2 s^{-1}$)</i>				
$H^* = 9.9 \times 10^{-13} \exp(9030/T)$	50	220-230	Williams and Golden, 1993	Kn-MS (i)
$H^* = 3.0 \times 10^{-4} \exp(4150/T)$	55	215-230		
$H^* = 1.3 \times 10^{-5} \exp(4640/T)$	60	200-230		
$HD_1^{1/2} = 3.6 \times 10^{-4} \exp(2060/T)$	59.6	200-220	Hanson and Ravishankara, 1993	CWFT-CIMS (j)
$HD_1^{1/2} = 1.1 \times 10^{-3} \exp(2070/T)$	55.6	205-225		
$HD_1^{1/2} = 9.2 \times 10^{-4} \exp(2440/T)$	50.5	200-230		
$H^* = 2.7 \times 10^{-4} \exp(4910/T)$	45	195-220		
$H^* = 1.0 \times 10^{-4} \exp(5110/T)$	45.3	195-220		
$H^* = 2.6 \times 10^{-4} \exp(4650/T)$	50	200-220		
$H^* = 6.8 \times 10^{-6} \exp(5310/T)$	51.1	200-220		
$H^* = 1.2 \times 10^{-5} \exp(6100/T)$	35	210-230	Zhang et al., 1993	Static (k)
$H^* = 6.5 \times 10^{-6} \exp(5880/T)$	40	200-230		
$H^* = 1.0 \times 10^{-6} \exp(5530/T)$	50	195-230		
$H^* = 4.2 \times 10^{-7} \exp(4920/T)$	60	195-210		
$H^* = 5.0 \times 10^{-4} \exp(5060/T)$	43	205-225	Elrod et al., 1995	Static (l)
$H^* = 1.2 \times 10^{-4} \exp(4940/T)$	50	205-225		
$H^* = 1.0 \times 10^3$	59.5	251	Hanson and Lovejoy, 1996 Hanson, 1998	RWFT-CIMS (c) RWFT-CIMS (m)
$H^* = 3.3 \times 10^{-5} \exp(5460/T)$	45	205-225		
$H^* = 6.9 \times 10^{-6} \exp(5450/T)$	50			
$HD_1^{1/2} = 1.4 \times 10^{-6} \exp(4230/T)$	49	230-260	Robinson et al., 1998	DT-TDLAS (d)
$HD_1^{1/2} = 9.8 \times 10^{-7} \exp(3900/T)$	54	230-260		
$HD_1^{1/2} = 4.8 \times 10^{-5} \exp(2500/T)$	59	235-265		
$HD_1^{1/2} = 7.9 \times 10^{-2}$	69	240		

Comments

- (a) The bulk substrate (1 mL to 5 mL) was cooled slowly to temperatures of 210 K to 230 K. The water vapour pressure was 5.3×10^{-4} mbar. Measured uptake coefficients did not depend on the appearance of the sample (glassy or crystalline). At 230 K, the measured uptake coefficient varied with aperture size, indicating diffusion limitation; the larger value is therefore listed as lower limit. The recovery yield of HCl was at maximum 5% when the solution was warmed to 253 K.
- (b) Droplet diameters were between 110 and 280 μm . The HCl concentration (circa 10^{12} molecules cm^{-3}) was measured downstream of the flow tube by tunable diode laser absorption.

The uptake coefficients listed in the table were corrected by gas phase diffusion using $D_{\text{HCl-He}} = 515 \text{ torr cm}^2 \text{ s}^{-1}$ and $D_{\text{HCl-H}_2\text{O}} = 120 \text{ torr cm}^2 \text{ s}^{-1}$. The time dependent uptake coefficient was evaluated in terms of solubility driven uptake. H^* was estimated by $H^* = HK_a/[H^+]$ at low H_2SO_4 concentrations and using the Hammett acidity concept to estimate the degree of dissociation of HCl in high wt % H_2SO_4 solution. For the liquid phase diffusion coefficient, $10^{-5} \text{ cm}^2 \text{ s}^{-1}$ was used.

- (c) Total uptake measurement over a known amount of H_2SO_4 solution (around 1 cm^3) in a rotating wetted wall flow tube coupled to a CIMS.
- (d) Time dependent uptake coefficients were measured using droplet diameters between 120 and 250 μm . The HCl concentration of about $10^{12} \text{ molecules cm}^{-3}$ was measured downstream of the flow tube by tunable diode laser absorption. The time dependent uptake coefficients were corrected for gas phase diffusion using $D_{\text{HCl-He}} = 0.701 \text{ atm cm}^2 \text{ s}^{-1}$, $D_{\text{HCl-Ar}} = 0.157 \text{ atm cm}^2 \text{ s}^{-1}$ and $D_{\text{HCl-H}_2\text{O}} = 0.166 \text{ atm cm}^2 \text{ s}^{-1}$. By varying the droplet size, the Kn numbers could be raised to 1 allowing determination of uptake coefficients in the range of 0.01 to 1. The corrected uptake coefficients were evaluated in terms of solubility driven uptake to determine of $H^*D_1^{1/2}$ and α_b .
- (e) Uptake of HCl was monitored through the size changes of 30 – 70 μm diameter droplets held in an electrodynamic trap with HCl pressures at 0.01 to 0.1 mbar. The time dependent uptake was evaluated to obtain an independent measurement of the diffusion coefficient. For data in the phase transfer limited regime, α_b was estimated from the slope of a plot of the rate of uptake versus the HCl partial pressure. The authors indicated that the HCl pressure was not homogeneous throughout the chamber, so that the α_b value reported is probably too low.
- (f) HCl containing molecular beams produced from the expansion of 2 % HCl in H_2 , 5% HCl in He or 10 % HCl in N_2 to result in beam energies of 105, 47 and 14 kJ/mol, respectively. The substrate was 70 % D_2SO_4 at 213 K. Fluxes were estimated to be below $10^{15} \text{ cm}^{-2} \text{ s}^{-1}$. Scattered or desorbing molecules were detected with a mass spectrometer at an exit angle of 45° . At the lowest energy, the fraction of in-elastically scattered molecules was less than 10%, from which we provide a lower bound to α_s reported in the table. Only 11% of those molecules trapped on the surface undergo proton exchange in the bulk of D_2SO_4 leading to the value of α_b listed in the table, if the proton exchange rate is limited by the solvation rate.
- (g) Molecular beam experiment using the same setup as in Morris et al. (2000), but covering a broader range of D_2SO_4 concentration. Again, the measured fraction of HCl undergoing proton exchange to DCl is interpreted as α_b assuming that α_s is close to 1, since inelastically scattered HCl molecules were not observed at low incident beam energies. The values given in the table were interpolated from the data provided as a plot only. A few experiments were also presented with DCl on H_2SO_4 , showing about 20% higher values, tentatively interpreted as isotopic effects. Behr et al. also provide values for the solubility based on HCl residence time measurement that are in line with Carslaw et al. (1995) at low acid concentration but are higher above 65 wt%.
- (h) Molecular beam experiment comparable to the setup used by Morris et al. (2000)
- (i) Time dependent HCl uptake coefficients measured in a Knudsen cell to derive values of $H^*D_1^{1/2}$. Values of H^* were obtained by estimating the temperature dependent diffusion coefficient from the measured temperature dependence of the viscosity. Initial uptake coefficients were not reported. The expressions given in the Table were obtained by fitting to the reported data.
- (j) Time dependent HCl uptake coefficients measured in a cylindrical flow tube with H_2SO_4 contained in a boat were analysed to derive values of $HD_1^{1/2}$. Direct measurements of H^* were done by static vapour pressure measurements. The parameters listed in the Table were obtained by fitting to the tabulated datasets given by Hanson and Ravishankara (1993). Initial uptake coefficients were not reported.
- (k) Static vapour pressure measurement using a mass spectrometer over a stirred $\text{H}_2\text{SO}_4/\text{HCl}/\text{H}_2\text{O}$ solution (0.01 – 5 wt % HCl). The expression given in the Table was obtained by fitting to the reported data.

- (l) Vapour pressure measurement over ternary and quaternary solutions in a wetted wall flow tube. The expression given in the Table was obtained by fitting to the reported data.
- (m) Vapour pressure measurement over H₂SO₄ solutions in a rotating wetted wall flow tube coupled to a CIMS. HCl was added to the solution at 10⁻² to 10⁻³ M. Linearity between HCl concentration and flow rate was checked to assure equilibrated conditions. The expression in the table is obtained from a fit to the data as reported. The value of H* reported in Table 1 of Hanson (1998) for the 50 wt % solution (1.36 x 10⁷) was corrected to 1.36 x 10⁶ to be consistent with the value plotted in the figure. Hanson (1998) also reanalysed data from Hanson and Ravishankara (1993) to take into account proper handling of the SF₆⁻ signal during CIMS calibration and a HCl background signal from memory effects on tubing downstream of the flow tube, which resulted in fair agreement with the newer measurements.

Preferred Values

Parameter	Value	T/K
α_s	>0.9	213 – 238
k_{sol}	$7.84 \times 10^{10} / \eta(\text{cP})$	190 – 300
k_{des}	$8.0 \times 10^{17} \exp(-5000/T)$	190 – 300
H* (M atm ⁻¹)	$(0.094-0.61X+1.2X^2) \exp(-8.68+(8515-10718X^{0.7})/T)$	190 – 300
c (cm ² cP K ⁻¹ s ⁻¹)	7.8×10^{-8}	190 – 300
A (M atm ⁻¹ K ^{1.43})	$169.5 + 5.18 (\text{wt}\%) - 0.0825 (\text{wt}\%)^2 + 3.27 \times 10^{-3} (\text{wt}\%)^3$	190 – 300
T_0 (K)	$144.11 + 0.166 (\text{wt}\%) - 0.015 (\text{wt}\%)^2 + 2.18 \times 10^{-4} (\text{wt}\%)^3$	190 – 300
<i>Reliability</i>		
$\Delta \log (\alpha_s)$	0.3	213 – 238
$\Delta \log (k_{sol})$	0.3	190 – 300
$\Delta \log (k_{des})$	0.3	190 – 300
$\Delta \log (H^*)$	0.3	190 – 300

Comments on Preferred Values

Uptake of HCl into H₂SO₄ solutions is fast. The molecular beam experiments provide the most direct measurement of the initial steps of HCl uptake. At low (close to thermal) incident beam energies, nearly all HCl molecules get thermally accommodated on the surface, evident from the absence of inelastically scattered molecules, leading to the recommended high value for α_s . The fraction of HCl molecules that actually undergo exchange with the bulk liquid phase can be tracked by observing proton exchanged DCI molecules desorbing from the surface. Assuming that solvation of HCl is the rate limiting step, this fraction is used to obtain the bulk accommodation coefficient α_b (Behr et al., 2009).

The kinetic data by Watson et al. (1990) did not allow to clearly differentiate the contributions by bulk accommodation and solubility. Robinson et al. (1998) provided a more reliable data set at lower temperature using the droplet train technique that involved sufficiently high Knudsen number conditions to extract large bulk accommodation coefficients. The Robinson et al. and Behr et al. data sets agree in that α_b is large (>0.6) up to moderate sulphuric acid contents. However, the temperature dependence observed is negative for the 39 and 48 wt% solutions above 230 K for the Robinson et al. data and positive for the 72 wt% solution below 240 K as obtained by Behr et al.. Robinson et al. interpret their negative T dependence as driven by the Gibbs free energy of the transition state at the surface. This would be inconsistent with the high single value measured by Hanson and Lovejoy (1996) at 274 K on a 34 wt% solution. Behr et al. (2009) use capillary wave theory to explain the strong negative correlation of α_b with viscosity (determining k_{sol}). Our recommendation follows the suggestion by Behr et al. (2009) for k_{sol} . We use an Arrhenius expression for k_{des} with an activation energy in between that of Behr et al. and Robinson et al.. Using

$$\alpha_b = k_{sol} / (k_{des} + k_{sol})$$

this leads to reasonable agreement with the data sets considered. It follows the strong negative dependence on sulphuric acid content at low T, whereby we prefer the newer Behr et al. (2009)

data with respect to the absolute value while still aligning it parallel to the concentration dependence of the earlier data. The recommended parameterization resolves the apparent inconsistency of positive temperature dependence at low temperature and high sulphuric acid concentration and negative temperature dependence for the more dilute solutions.

In the absence of a reactive sink in the aqueous phase, uptake is driven by solubility, characterized by the effective Henry's Law constant H^* and the diffusion coefficient, D_1 .

The more reliable solubility values are derived from experiments, in which the solubility was directly measured: Elrod et al. (1995); Hanson (1998) and the one data point by Hanson and Lovejoy (1996). The Zhang et al. (1993) data are likely too low due to HCl calibration issues as noted by Elrod et al.. Many kinetic experiments were analysed in terms of solubility limited uptake to obtain $H^*D^{1/2}$. This requires estimating diffusion coefficients to obtain H^* , which in turn are parameterized in terms of the viscosity. We recommend using the parameterization presented by Shi et al. (2001), which fits well to data by Williams and Long (1995) but extends into tropospherically more relevant dilute solutions at high T:

$$\eta = AT^{-1.43} \exp(448K / (T-T_0))$$

The temperature and concentration dependent diffusion coefficient can then be obtained by the Stokes-Einstein equation

$$D_1 = c T / \eta$$

The diffusion coefficients of HCl thus obtained are in reasonable agreement with data obtained by Klassen et al. (1998), but in some disagreement with measurements at $T < 190$ K by Schwell et al. (2000), though at only two acid concentrations. Schwell et al. argue that the Stokes Einstein approach used by Klassen et al. may underestimate the diffusion coefficient at temperatures below 200 K.

This procedure to obtain H^* from the measured $HD^{1/2}$ values leads to fair agreement with the directly measured H^* values and aligns the higher temperature droplet train experiments by Robinson et al. (1998) to those at lower T.

We recommend the mole fraction based expression by Shi et al. (2001) for H^* over 190 – 300 K for up to 70 wt% solutions ($X = (\text{wt}\%) / ((\text{wt}\%) + (100 - (\text{wt}\%))98/18)$) noting the potential formation of HSO_3Cl as suggested by Robinson et al. (1998) to explain the higher H^* at > 70 wt% solution. Shi's parameterization builds upon the thermodynamic models of Carslaw et al. (1995) and Luo et al. (1995) and uses an expression modified from that used by Hanson (1998).

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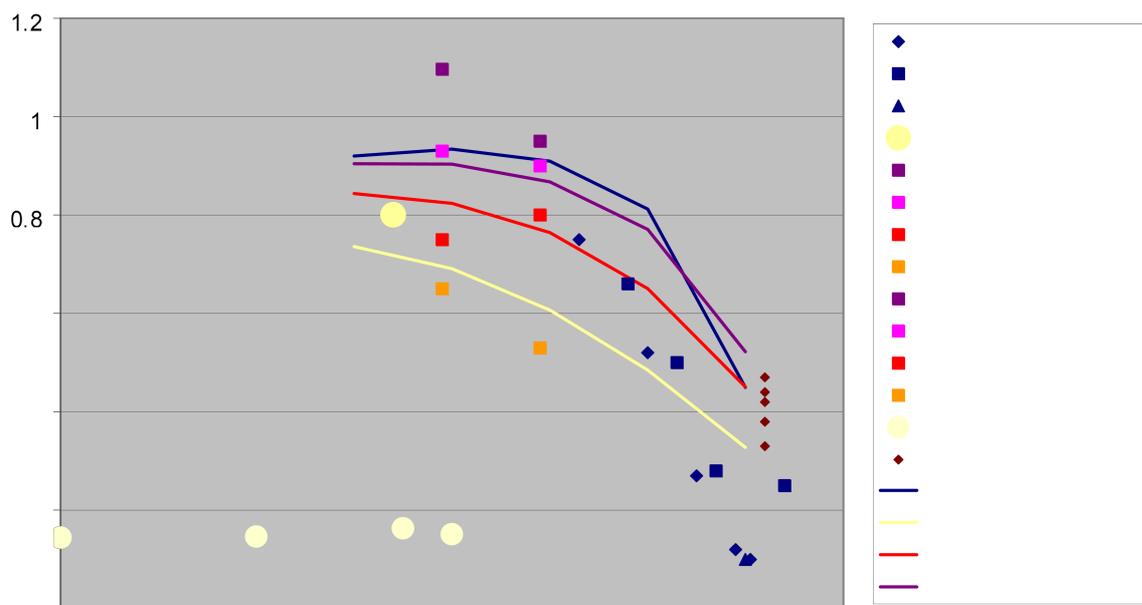


Figure 1: Bulk accommodation coefficient, α_b , as a function of sulphuric acid concentration

