

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet VI.A4.17 HET_SL_17

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The citation for this data sheet is: IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, <http://iupac.pole-ether.fr>.

This data sheet last evaluated: June 2010; last change in preferred values: June 2010.

HBr + H₂SO₄ → products

Experimental data

Parameter	Temp./K	Reference	Technique/ Comments
<i>Solubility: H* (M atm⁻¹)</i>			
log(<i>H*</i>) = 2680 / <i>T</i> – 5.00 (54 wt.% H ₂ SO ₄)	200 - 240	Williams et al., 1995	Knudsen-MS (a)
log(<i>H*</i>) = 2480 / <i>T</i> – 4.93 (60 wt.% H ₂ SO ₄)			
log(<i>H*</i>) = 2680 / <i>T</i> – 4.87 (66 wt.% H ₂ SO ₄)			
log(<i>H*</i>) = 2680 / <i>T</i> – 4.80 (72 wt.% H ₂ SO ₄)			
5.95 × 10 ⁶ (59.6 wt. % H ₂ SO ₄)	210	Abbatt, 1995	CWFT-MS (b)
log(<i>H*</i>) = 2900 / <i>T</i> – 3.8 (40.3 wt.% H ₂ SO ₄)	218 - 298	Abbatt and Nowak, 1997	CWFT-MS (c)
log(<i>H*</i>) = 2800 / <i>T</i> – 4.9 (48.8 wt.% H ₂ SO ₄)			
log(<i>H*</i>) = 2400 / <i>T</i> – 4.5 (59.6 wt.% H ₂ SO ₄)			
log(<i>H*</i>) = 2400 / <i>T</i> – 4.9 (50.5 wt.% H ₂ SO ₄)			
log(<i>H*</i>) = 2500 / <i>T</i> – 5.8 (64.4 wt.% H ₂ SO ₄)			
log(<i>H*</i>) = 2200 / <i>T</i> – 5.8 (69.8 wt.% H ₂ SO ₄)			
see comment and preferred values	195 - 250	Kleffmann et al., 2000	(d)
<i>Diffusion coefficient: D₁ (cm² s⁻¹)</i>			
7.9 × 10 ⁻⁸ <i>T</i> /η (30-72 wt.% H ₂ SO ₄)	220-300	Klassen et al., 1998	(e)

Comments

- (a) Values of $HD^{0.5}$ were extracted from time dependent HBr uptake to H₂SO₄ films of 59.8, 66.1 and 71.9 wt.% and at temperatures between 200 and 240 K. Values of $HD^{0.5}$ were converted to solubilities using diffusion coefficients calculated using $D = CT / \eta$ where η is the viscosity of H₂SO₄ (taken from Williams and Long, 1995) and C was estimated to be 1×10^{-7} cm² cP/sK. This value of c compared well to later measured values (Klassen et al., 1998). Experiments were also conducted by measuring the vapour pressure of HBr above its solution (at known concentration) in H₂SO₄ at 54, 60 and 66 wt. %.

- (b) Values of $HD^{0.5}$ were extracted from time dependent HBr uptake to H_2SO_4 films of 59.6, 64.4 and 69.8 wt.% and at temperatures between 233 and 200 K. H was extracted using diffusion coefficients for HBr in H_2SO_4 as described by Williams et al., (1995) (see comment (a)). Only the result for $HD^{0.5}$ at 210 K (59.6 wt.%) was listed though data were obtained over the temperature / concentration range indicated. The solubility listed was calculated using temperate and concentration dependent diffusion coefficients of Klassen et al. (1998).
- (c) Equilibrium concentrations of HBr were measured above cold, HBr-containing H_2SO_4 samples of know HBr concentration composition and wt.% (40.3 – 60.5 %). Solubility data at room temperature were obtained by bubbling N_2 through a HBr / H_2SO_4 solution of known composition and analysing the HBr mole fraction in the gas by re-dissolution in H_2O with electrical conductivity measurement of ion concentrations. The data listed also contain a parameterisation of measurements (at 59.6, 64.4 and 69.8 wt.%) reported in Abbatt (1995), and described in comment (b).
- (d) Head space above stirred, bulk solutions of known composition was analysed by tuneable diode laser absorption spectroscopy of HBr. H_2SO_4 solutions of 53 – 75 wt.% were used.
- (e) Modified diaphragm cell method. The value of the parameter C was independent of the H_2SO_4 concentration and agrees well (within 5 %) with calculations using the Wilke and Chang (1955) expression.

Preferred Values

Parameter	Value	T/K
m_1 (wt.% ⁻² K)	-1.977×10^{-4}	
m_2 (wt.% ⁻¹ K)	-2.096×10^{-2}	
m_3 (K)	4.445	
b_1 (wt.% ⁻²)	-8.979×10^{-5}	
b_2 (wt.% ⁻¹)	2.141×10^{-2}	
b_3	-6.067	
C (cm ² cP K ⁻¹ s ⁻¹)	7.9×10^{-8}	220 - 300
A	$169.5 + 5.18 (\text{wt}\%) - 0.0825(\text{wt}\%)^2 + 3.27 \times 10^{-3}(\text{wt}\%)^3$	
T_0	$144.11 + 0.166(\text{wt}\%) - 0.015(\text{wt}\%)^2 + 2.18 \times 10^{-4} (\text{wt}\%)^3$	
<hr/>		
<i>Reliability</i>		
$\Delta \log H^*$	0.3	

Comments on Preferred Value

The available data on the interaction of HBr with H_2SO_4 solutions indicates very high solubility, especially in dilute solutions and at low temperatures. Efficient dissociation of HBr in H_2SO_4 implies that the solubilities are effective (H^*). Data have been obtained using static or stirred samples with head-space analysis or using time dependent uptake coefficients in combination with diffusion coefficients of HBr in H_2SO_4 . Most authors estimate the overall uncertainty as being better than a factor of two, which is borne out by the reasonable agreement from group to group. Kleffmann et al. (2000) have analysed the experimental datasets to produce a H_2SO_4 concentration and temperature dependent parameterisation of HBr effective solubility. This is adopted in our table of preferred values in which:

$$\log_{10} H^* = 1000 m / T + b \quad \text{where}$$

$$m = m_1[H_2SO_4]^2 + m_2[H_2SO_4] + m_3 \text{ and } b = b_1[H_2SO_4]^2 + b_2[H_2SO_4] + b_3$$

and the H₂SO₄ concentration [H₂SO₄] is in wt.%

Note that the experimentally derived solubilities are factors of 2-6 lower than those calculated using activity coefficients (Luo et al., 1995).

Klassen et al (1998) have parameterised the diffusion coefficient for HBr in H₂SO₄ as:

$$D_1 = CT / \eta$$

where C is a constant (cm² cP K⁻¹ s⁻¹) and η is the viscosity of H₂SO₄ at a given wt.% and temperature. Shi et al., have taken viscosity data from Williams and Long (1995) and for pure water to derive an extended formulation to cover H₂SO₄ viscosities from 0 to 80 wt%., which can be used with the C constant above to derive D_1 over the same concentration range using:

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

This parameterisation results in values of η which agree to better than 10 % (for 40 – 70 wt.% H₂SO₄ solutions) with those of Klassen et al. (1998).

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