IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet V.A1.30 HI30

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: January 2008; last change in preferred values: January 2008.

HBr + ice

Experimental data

Parameter	Temp./K	Reference	Technique/Comments
Experimental uptake coefficients: γ, γ₀			
γ_{ss} = 0.3-1.0	201	Hanson and Ravishankara, 1992	CWFT-CIMS (a)
γ_{ss} = 0.41 ± 0.15 γ_{ss} = 0.30 ± 0.11 γ_{ss} = 0.25 ± 0.6	180 190 200	Seisel and Rossi, 1997	Knud-MS (b)
γ_0,γ_{ss} = 0.33 ± 0.02 γ_0,γ_{ss} = 0.27 ± 0.03 γ_0,γ_{ss} = 0.22 ± 0.02	190 200 210	Flückiger *et al*., 1998	Knud-MS (c)
γ_0,γ_{ss} = 0.03±0.005 γ_0,γ_{ss} = > 0.1	212-233 <212	Percival, Mössinger and Cox, 1999	CWFT-MS (d)
γ_0 = 0.18±0.065 γ_0 = 0.07±0.02 γ_0 = 0.04±0.01	181 200 227	Chu, Diao and Chu, 2000	CWFT-MS (f)
γ_0 = 0.24 ± 0.05 γ_0 = 0.61 ± 0.06	100 140	Hudson et al., 2001	(f)
Partition coefficients			
$K = 4.15 \times 10^5$ (cm^{-1})	188	Chu, and Chu, 1999	CWFT-MS (g)

Comments

(a) Ice layers 2 - 10 μm thick were condensed from the vapour phase onto the cold flow tube wall and doped with HNO_3 for NAT studies. The uptake of HBr on pure ice is very efficient with no signs of saturation. It is thought that a new fluid binary phase: HBr-H_2O, forms.
(b) Uptake of pure HBr on vapour-condensed ice films and on bulk aqueous solutions of H_2SO_4. [HBr] = (2 - 8) x 10^{11} molecule cm^{-3}. No saturation effects observed.
(c) [HBr] = (2 – 8) x 10^{11} molecule cm^{-3}; vapour condensed ice. Transient pulsed-dose as well as steady-state experiments with HBr at molecular densities of (5.6 - 560) x 10^{10} molecules cm^{-3}. The temperature dependence confirmed the strong negative effect observed by Seisel and Rossi.[2] However, the formation of stoichiometric hydrates could not be confirmed.
(d) Frozen film ice. The HBr concentrations were in the range (1-30) x 10^{12} molecule cm^{-3} and the γ values were independent of concentration. No evidence for saturation.
(e) Uptake experiment using a laminar flow tube equipped with mass spectrometric detection. P_{HBr} was 1x10^{-6} Torr in 0.5 Torr of He. The tabulated values are taken from Fig.7 of the cited paper and have not been corrected using pore diffusion theory.
(f) The uptake coefficient of HBr on ice was determined using single-shot laser-induced thermal desorption by IR laser radiation from HBr/H_2O multilayer films of 140A thickness deposited on an Al_2O_3 substrate monitored by residual gas MS. HBr pressure between 3x10^{-8} to 1.4x10^{-7} Torr led to low HBr coverages. Absolute HBr coverages have been obtained using HeNe interferometric techniques.
(g) Uptake of HBr into vapour deposited ice films measured as a function of P_{HBr} over range (0.44 – 51)x10^{-7} Torr in 0.5 Torr of He, without compensating water flow. Continuous uptake was observed until film became saturated and desorption of HBr was observed; the film evaporated at this point. Integrated uptake was represented as a function of HBr pressure by a power function: $P_{HBr} = K q^{f}$, with f = 0.83 ± 0.05 and K = (5.1 ± 4.7) x $10^{-20}cm^{-2}$ $molecule^{-1}$. Uptake amount also increased with film thickness. Thickness dependence of the amount of HBr taken up into 0.5 – 10 mm films was fitted with an ice micro-granule model (Keyser et al.) to obtain "true" surface coverage θ_o of 1.1 × 10^{15} , 6.1 × 10^{14}, and 2.9 × 10^{14} molecules cm^{-2} for P_{HBr} = 1.0 × 10^{-6} , 5.2 ×10^{-7} , and 2.2 × 10^{-7} Torr, respectively. HCl–HBr co-adsorption experiments showed that uptake of both acids was reduced by competition for surface sites.

Preferred Values

Parameter	Value	T/K
γ	1 x 10^{-5} exp(840/T)	180 - 240
K_{LinC} / cm	4.14 x 10^5	188
Reliability		
Δ log (γ)	± 0.2	298
Δ (K_{LinC}) / cm	± 0.3	298
Δ (E/R) /K	± 500	200-298

Comments on preferred values

Several groups have measured the uptake coefficient for HBr on ice films over a range of temperature. All studies report continuous uptake with no apparant saturation of the ice surface and this is attributed to formation of HBr hydrates, HBr.nH2O (n = 2 or 3), which are incorporated into the surface layers of the ice film. The values of the uptake coefficient and the temperature dependence are in poor agreement, the differences probably resulting partly from the differences in the morphology the ice films. Nevertheless we recommend an

Arrhenius expression for the temperature dependence of γ, obtained by fitting the data of Hanson and Ravishankara, (1992), Seisel and Rossi, (1997), Flückiger, et al (1998), Percival, et al (1999), and Chu et al. (2000). The uncertainty on the E/R is estimated.

Chu and Chu (1999) have reported comprehensive measurements of HBr uptake at 188 K. No evidence was found for reversible uptake, the uptake amounts increasing monotonically with P_{HBr} and greatly exceeding single monolayer (ML) coverage for geometric surface area. This is attributed to pore diffusion and hydrate formation. Uptake amounts at the thin film limit cited in comment (f) were obtained after correction using a pore diffusion model and are still up to a factor of 5 larger than the typical maximum surface coverages for monolayer adsorption on an ice surface at temperatures around 200K. Thus uptake amounts cannot be described by the Langmuir model, and are best described by an isotherm of the form $\theta = K[HBr]^f$ (molecule cm^{-2}). The recommended partition coefficient for HBr on ice is obtained by fitting the corrected surface coverages at 188K reported by Chu and Chu (1999) to this isotherm. The best fit gave $K = (4.14 \pm 0.11) \times 10^5$ $cm^{-1}$and $f = 0.88 \pm 0.01$. K can be considered a measure of the solubility of HBr in ice.

References

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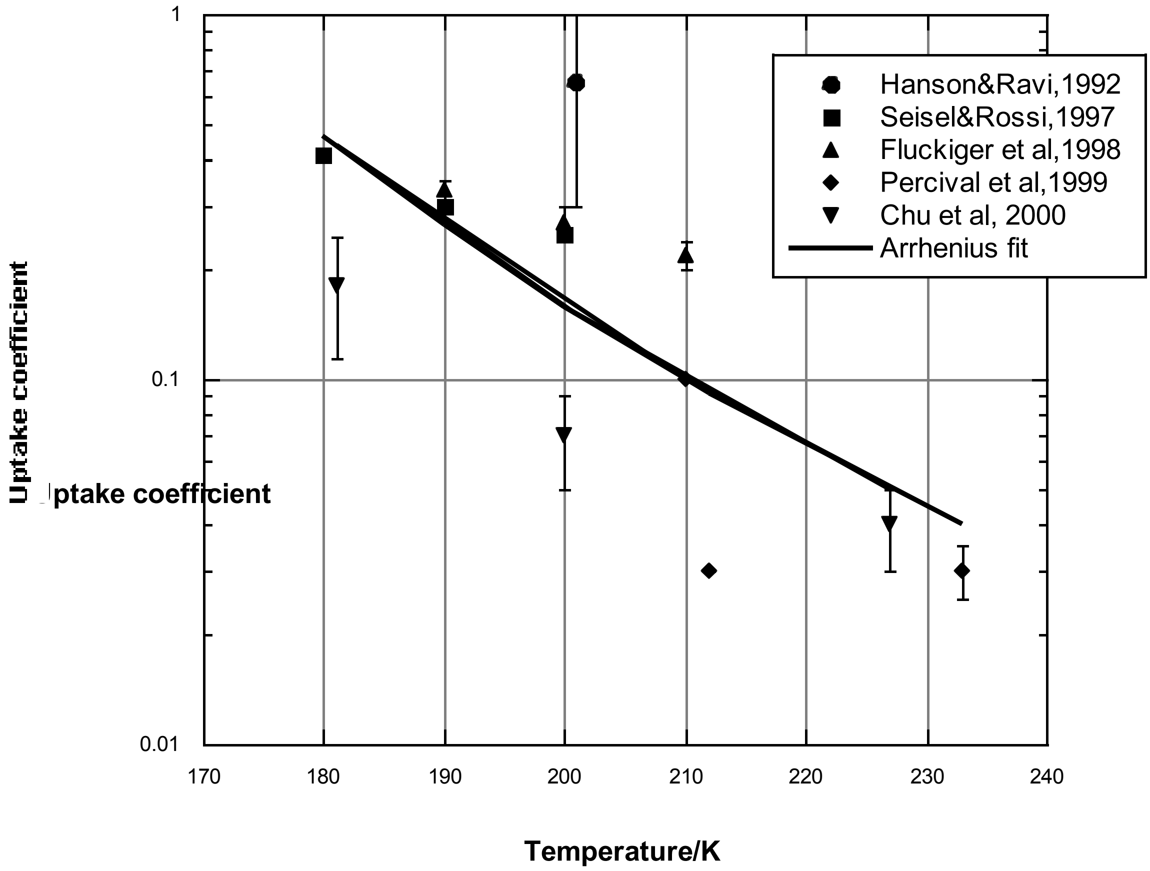

Fig 1 Uptake coefficients for HBr on ice; Hanson and Ravishankara; Fluckiger et al, Percival et al, Chu et al;

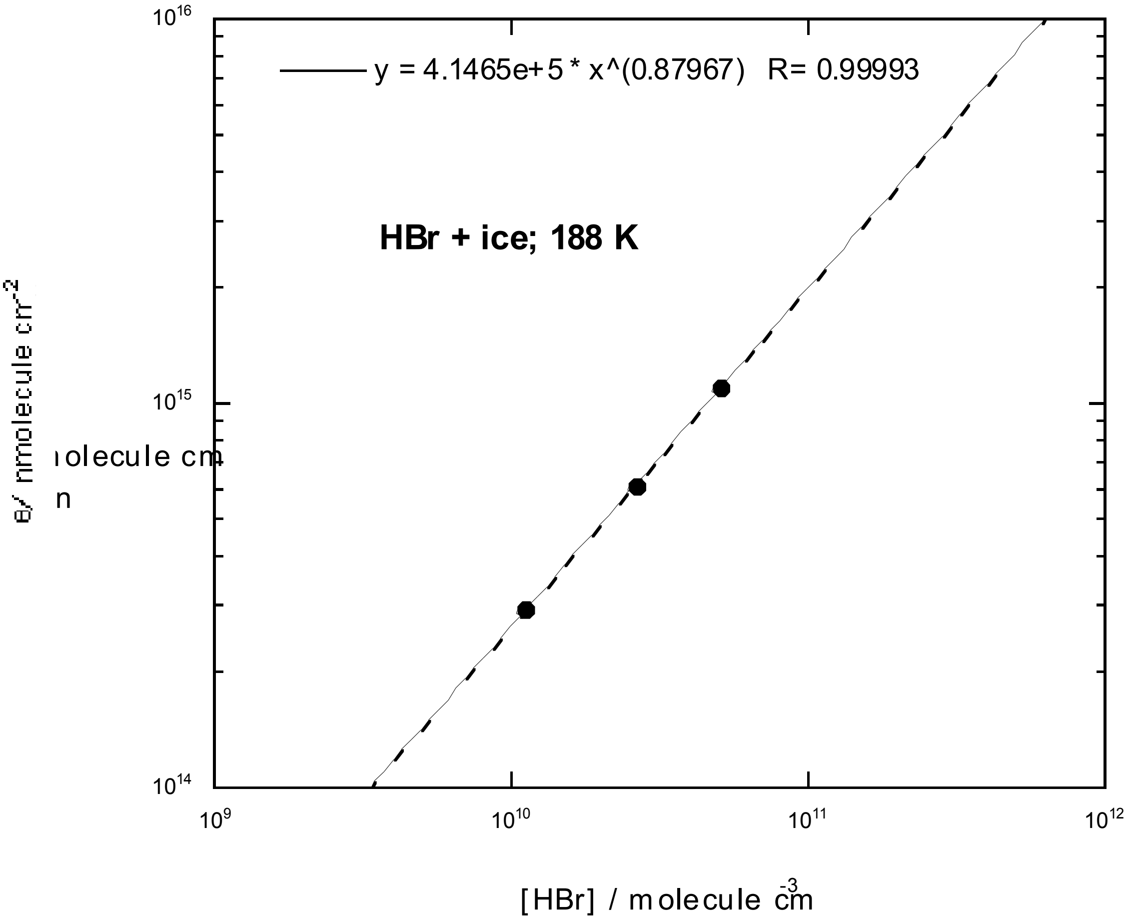

Fig.2 Absorption isotherm for HBr uptake on ice film at 188 K