

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet VI.A2.16 HET_SALTS_16

Data sheets can be downloaded for personal use only and must not be retransmitted or disseminated either electronically or in hard copy without explicit written permission.

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 to preferred values: June 2010.



Experimental data

| Parameter | aqueous solution | Temp./K | Reference | Technique/ Comments |
|--|--|-----------|-----------------|------------------------|
| <i>Uptake coefficients, γ</i> $\approx 4 \times 10^{-3} - 0.16$ | Br ⁻ ($1.25 \times 10^{-3} - 0.5$ M) | 263 - 293 | Hu et al., 1995 | DT-MS (a) |

Comments

- (a) Flow tube at 8 – 27 mbar He (+ H₂O) with 120 – 250 μm droplets. Cl₂ ($5 - 100 \times 10^{12}$ molecule cm⁻³) was detected by mass spectrometer. The size of the uptake coefficient and its dependence on the bromide concentration could not be explained if only a bulk reaction was considered.

Preferred Values

| Parameter | Value | T/K |
|--|-------------------------------------|-----------|
| α_b | 1 | 260 - 295 |
| α_s | 1 | 260 - 295 |
| $k_{(\text{Br}^-)}$ (M ⁻¹ s ⁻¹) | $4.58 \times 10^{14} \exp(-2866/T)$ | 260 - 295 |
| H (M atm ⁻¹) | $1.44 \times 10^{-6} \exp(3181/T)$ | 260 - 295 |
| D_l (cm ² s ⁻¹) | $0.127 \exp(-2645/T)$ | 260 - 295 |
| R (L atm mol ⁻¹ K ⁻¹) | 8.2057×10^{-2} | |
| $k_s \cdot K_{\text{LangC}} \cdot N_{\text{max}}$ (L mol ⁻¹ cm ⁻¹ s) | $4.92 \times 10^{-4} \exp(4134/T)$ | 260 - 295 |
| <i>Reliability</i> | | |
| $\Delta \log(\gamma)$ | ± 0.3 | 260 - 295 |

Comments on Preferred Values

The only data available for the uptake of Cl₂ to bromide containing, aqueous solutions is that of Hu et al., (1995). They showed that the uptake of Cl₂ could not be explained by bulk phase reaction alone (high values of measured γ and non-linear plot of inverse γ versus $[\text{Br}^-]^{-0.5}$) and proposed that reaction within a surface-near volume was responsible. In this case, the measured uptake coefficient (γ) is given by:

$$\frac{1}{\gamma} = \frac{1}{\alpha_s} + \frac{1}{\Gamma_s + \left(\frac{1}{\Gamma_{sb}} + \frac{1}{\Gamma_b} \right)^{-1}}$$

where:

$$\Gamma_s = \frac{4k_s a_{(Br^-)} K_{LangC} N_{max}}{\bar{c}(1 + K_{LangC} [Cl_2])} \quad \text{and}$$

$$\Gamma_b = \frac{4HRT}{\bar{c}} \sqrt{D_l k_{(Br^-)} a_{(Br^-)}}$$

and $a_{(Br^-)}$ is the activity (mol L⁻¹) of the dissolved bromide ion.

For efficient interfacial mass transport, $\alpha_s = \alpha_b = 1$ the first equation simplifies to:

$$\frac{1}{\gamma} = 1 + \frac{1}{\Gamma_s + \Gamma_b}$$

When far from surface saturation (low K_{LangC} or low $[Cl_2]$) the second expression also reduces to:

$$\Gamma_s = \frac{4k_s a_{(Br^-)} K_{LangC} N_{max}}{\bar{c}}$$

The units of the composite term $k_s \cdot K_{LangC} \cdot N_{max}$ are L mol⁻¹ cm⁻¹ s if the surface concentration of bromide ions is considered (as in this case) to be proportional to the bulk activity (mol L⁻¹). The depth though which the surface reaction is considered to take place is integrated in the values of $k_s \cdot K_{LangC} \cdot N_{max}$, which were derived by fitting to experimental data.

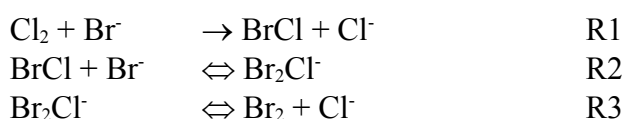
The temperature dependence of Γ_s can arise from both the partition coefficient of Cl₂ to the surface (K_{LangC}) or via the surface rate coefficient (k_s), though the former is expected to dominate. The parameterisation gives values of γ that are consistent with those presented by Hu et al. (1995) at all temperatures and bromide activities covered in their experiments. Diffusive effects were also taken into account when fitting to the experimental datasets by using

$$\frac{1}{\gamma} = 1 + \frac{1}{\Gamma_{diff}} + \frac{1}{\Gamma_s + \Gamma_b}$$

and effective gas-phase diffusion coefficients for Cl₂ reported by Hu et al.

The tabulated, temperature dependent expressions for aqueous phase rate coefficients, solubilities and aqueous phase diffusion coefficients listed for calculation of Γ_b were calculated from values given by Hu et al. (1995) at single temperatures. These values were taken in preference to other reports (e.g. of $k_{(Br^-)}$ by Wang et al., 1994) in order to maintain an internally consistent set of parameters. Note that γ has almost no sensitivity to α as at high values of the uptake coefficient (when α may be rate limiting) the surface reaction dominates. At low uptake rates, the bulk-phase chemical reaction dominates and the effect of α is diminished.

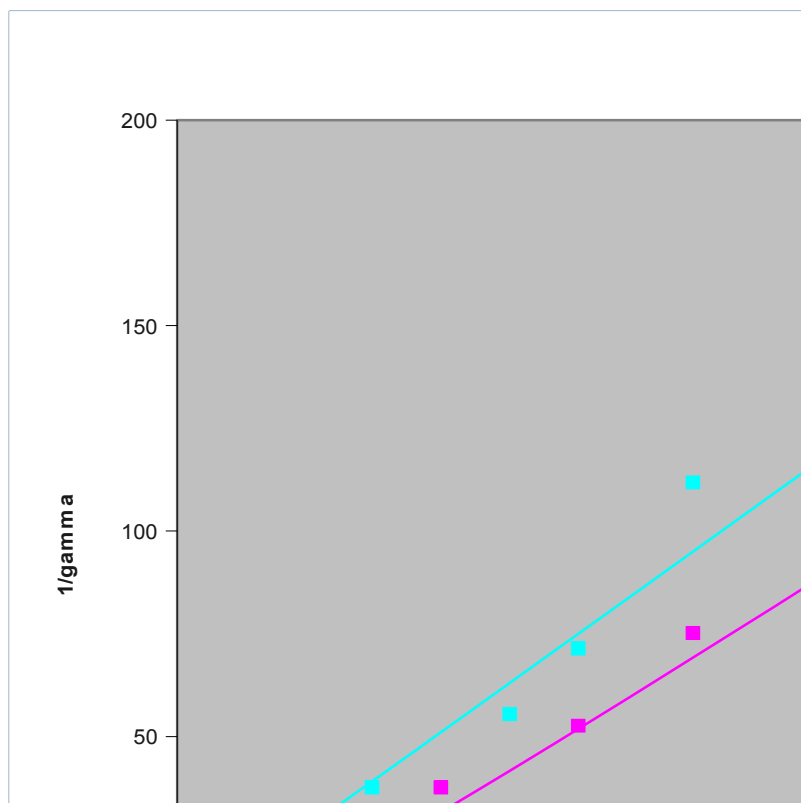
Studies of the uptake of Cl₂ to dry and frozen bromide containing salts surfaces have identified Br₂ and BrCl as the main products released to the gas-phase (Berko et al., 1991; Mochida et al., 1998; Huff and Abbatt, 2000; Adams et al., 2002; Santschi and Rossi., 2004). BrCl is formed initially and is converted to Br₂ by reaction with Br⁻. The same products are expected for the reaction on in an aqueous surface, with the ratio of BrCl to Br₂ defined by aqueous phase equilibria:



References

Adams, J. W., Holmes, N. S. and Crowley, J. N.: Atmos. Chem. Phys. 2, 79-91, 2002.

Berko, H. N., McCaslin, P. C. and Finlayson-Pitts, B. J.: J. Phys. Chem. 95, 6951-6958, 1991.
Hu, J. H., Shi, Q., Davidovits, P., Worsnop, D. R., Zahniser, M. S. and Kolb, C. E.: J. Phys. Chem. 99, 8768-8776, 1995.
Huff, A. K. and Abbatt, J. P. D.: J. Phys. Chem. 104, 7284-7293, 2000.
Mochida, M., Hirokawa, J., Kajii, Y. and Akimoto, H.: Geophys. Res. Lett. 25, 3927-3930, 1998.
Santschi, C. and Rossi, M. J.: Phys. Chem. Chem. Phys. 6, 3447-3460, 2004.
Wang, T. X., Kelley, M. D., Cooper J. N. and Margerum, D. W.: Inorg. Chem. 33, 5872, 1994.



Measured uptake coefficients for Cl_2 to bromide solutions from Hu et al (1995). Except for ion activities of 0.35 M, the datapoints were read from a graph. The solid lines are calculated using the parameters and equations listed above.