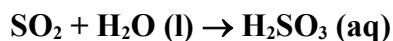


IUPAC Task Group on Atmospheric chemical Kinetic Data Evaluation – Data Sheet VI.A1.10 HET_H2OL_10

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Data sheet last evaluated: March 2011; last change in preferred values: March 2011.



Experimental data

Parameter	Temp./K	Reference	Technique/ Comments
γ_0 0.054±0.006 (init. droplet pH = 11.5)	295	Gardner et al., 1987, 1989	DT-TDL (a)
$\gamma_0 = 0.12$ 0.11±0.2 (init. droplet pH = 11.5)	260-292	Worsnop et al., 1989	DT-TDL (b)
8.0x10 ⁻³ (droplet pH = 0 to 2) 0.11 (droplet pH > 6)	283	Jayne et al., 1990	DT-TDL (c)
0.06 (+0.14, -0.03)	300	Welter et al., 1990	LJ-IC (d)
$\gamma_0 = 0.13±0.01$	298	Ponche et al., 1993	DT-IC (e)
0.028±0.010 7.7x10 ⁻³	293.5	Shimono and Koda, 1996	(f)

Comments

- (a) Uptake of SO₂ into a fast moving train of water droplets (80 to 180 μm diam). [SO₂] ((1.5 - 15.0) x 10¹² molecule cm⁻³) was measured by diode-laser adsorption. Surface saturation effects were shown to be absent at [SO₂] and initial pH used. Measurements of aqueous [S(IV)] in exposed droplets confirmed uptake coefficient values determined from SO₂ loss. Correction for gas phase diffusion to a static drop gives the cited value of γ_0 , the mass accommodation coefficient.
- (b) Experiment designed to determine the temperature-dependent mass accommodation coefficients of SO₂ and H₂O₂ on aqueous surfaces, using oxidation of HSO₃²⁻ to overcome solubility limitation of S(IV) uptake. 200 mm diam. water droplets with [SO₂]₀ = 1 x 10¹³ molecule cm⁻³ at 260 - 292 K. Uptake coefficients were corrected for gas diffusion. At low pH, γ decreased with droplet exposure time due to reduced solubility of S(IV), and increased with pH. Temperature dependence of the initial uptake coefficient γ_0 was given by the expression: $\gamma_0 / (\gamma_0 - 1) = A \exp(-\Delta E/RT)$ with $A = 4 \times 10^{-2}$ and $\Delta E = -2 \pm 5 \text{ kJ mol}^{-1}$. The value of γ_0 equates to the mass accommodation coefficient α_b .
- (c) details as (b). Uptake measured for a range of initial pH in the bulk droplets from 0 to 12 and at [SO₂]₀ of 10¹³ and 10¹⁵ molecule cm⁻³. Corrections for gas phase diffusion and additional acidification of the droplet due to SO₂ adsorption were applied to the uptake kinetics. The γ_0 values displayed in the Table are corrected values obtained at minimal droplet-gas interaction

time (2 ms) and minimum SO₂ density (10¹³ molecule cm⁻³). The observed uptake rates over the pH range were significantly greater than predicted on the basis of the known rate of SO₂ reaction in bulk liquid water at pH>5 and known Henry solubility at low pH. A mechanism involving formation of a surface complex HSO₃⁻-H⁺ was proposed. They derive kinetic and thermodynamic parameters governing these surface interactions.

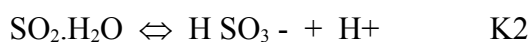
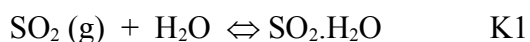
- (d) Liquid jet of water (100 μm diameter); H₂O₂ was added in order to rapidly oxidize SO₂ (typically 100 ppm) to sulfate. The uptake kinetics of SO₂ was measured by analysis of the sulfate concentration in the collected jet water using ion chromatography. Retrieval of γ used a gas diffusion model to define gas-surface collision rate. The uptake was found to be dependent on [SO₂] due to a change in surface pH. Addition of NH₃ to the SO₂/air mixture minimized the pH dependence.
- (e) Uptake into droplet train of [SO₂] = 2.8 to 28 ppmv. Dilute aqueous H₂O₂ was added to the condensed phase to rapidly oxidize dissolved SO₂ to H₂SO₄. Uptake monitored by chemical analysis of the collected aqueous sulphate by ion chromatography. The observed uptake coefficient γ is strongly dependent on the initial pH of the droplet in the range 4 to 11 and, at pH < 11, on the interaction time. Cited value of γ_0 which is independent of pH is corrected for gas phase diffusion and represents the mass accommodation coefficient. (The uncorrected γ_0 at t = 0 was 0.060 ± 0.008).
- (f) Uptake measurement of SO₂ on counterflowing liquid H₂O using LIF detection of SO₂ excited at 224.34 nm. The range of [SO₂] was between 3.3 × 10¹¹ and 1.7 × 10¹⁴ molecule cm⁻³ in the temperature range 280-305 K at an average contact time of 37 ms and a total pressure range of 37-131 mbar. γ was determined from the concentration dependence of SO₂ in the impinging flow field and was found to strongly depend on the pH of the condensed phase.

Preferred values

Parameter	Value	T/K
α_s	1	260 - 298
k_{des} (s ⁻¹)	5.8 × 10 ⁴	260 - 298
k_{sb} (s ⁻¹)	1.3 × 10 ⁴	260 - 298
N_{max} (cm ⁻²)	10 ¹⁴	260 - 298
K_{LinC} (cm)	0.13	260 - 298
k^l /s ⁻¹	no recommendation (see discussion)	
<i>Reliability</i>		
$\Delta\log(\alpha_s)$ (s ⁻¹)	1	260 - 298
$\Delta\log(k_{des})$ (s ⁻¹)	1	260 - 298
$\Delta\log(k_{sb})$ (cm ⁻²)	1	260 - 298
$\Delta\log(N_{max})$ (cm)	0.3	260 - 298
$\Delta\log(K_{LinC})$ (cm)	0.3	260 - 298

Comments on Preferred values

When SO₂ is adsorbed at the surface and enters aqueous solution it reacts with water molecules and an equilibrium is set up between the forms of S(IV): hydrated SO₂, HSO₃⁻ and SO₃²⁻ via the following equilibria:



where

$$H = \frac{[\text{SO}_2 \cdot \text{H}_2\text{O}]}{p(\text{SO}_2)}$$

$$K_1 = \frac{[H^+][HSO_3^-]}{[SO_2 \cdot H_2O]}$$

and

$$K_2 = \frac{[H^+][SO_3^{2-}]}{[HSO_3^-]}$$

which gives in turn:

$$\begin{aligned} [S(IV)]_{total} &= p(SO_2) H \times \left\{ 1 + \frac{K_1}{[H^+]} + \frac{K_1 K_2}{[H^+]^2} \right\} \\ &= p(SO_2) \cdot H^* \end{aligned}$$

This leads to the mole fractions and total dissolved S(IV) being a strong function of pH. Thus the effective Henry's solubility constant, H^* , decreases with pH. Over the pH range typical of atmospheric droplets (pH 2 to 6), most dissolved SO_2 is in the form of HSO_3^- .

Following the usual formalism for the resistance model the net uptake coefficient of SO_2 to an aqueous surface is given by:

$$\gamma_{net} = \left(\frac{1}{\alpha_b} + \frac{1}{\Gamma_{sol} + \Gamma_b} \right)^{-1}$$

In the absence of chemical reaction in solution uptake is solubility limited, and the time-dependent resistance term for uptake into the diffusion-limited shell in the droplet is given by:

$$\Gamma_{sol} = \frac{4RTH^*}{c} \left(\frac{D_l}{t} \right)^{1/2} \quad (1)$$

In laboratory experiments the effect of aqueous chemistry on H^* was found to lead to a strong dependence of the uptake coefficient on pH. In addition acidity due the H^+ from hydrolysis of SO_2 taken up into the surface layer, leading to lower effective surface pH, needs to be accounted for in the uptake kinetics. Assuming that gas-phase SO_2 is in equilibrium with $SO_2(aq)$ at the liquid surface and neglecting the second dissociation involving K_2 , the actual $[H^+]$ at the surface is given by:

$$[H^+] = H' \pm \left(H'^2 + K_w + K_1[SO_2] \right)^{1/2}$$

where

$$H' = \frac{1}{2} \left([H^+]_0 - \frac{K_w}{[H^+]_0} \right)$$

Literature values for the Henry's constant, H , for SO_2 , and for the dissociation constants $K_w (=10^{14} M^2)$ for water, and K_1 and K_2 , for bisulphite and sulphite ions respectively, are taken from Goldberg and Parker (1985):

$H/M \text{ bar}^{-1}$	$3.42 \times 10^{-5} \exp(3133/T)$	273-300
K_1/M	1.4×10^{-2}	298
K_2/M	6.5×10^{-8}	298
$D_1(SO_2.aq) / \text{cm}^2\text{s}^{-1}$	8×10^{-6}	283

These are used to compute the effective solubility H^* for a specified pH, taking into account the effect of dissolved SO_2 (as described in Worsnop et al, 1989, and Ponche et al., 1993).

In alkaline droplets (e.g. pH = 11) surface saturation of SO₂ is negligible and γ is time independent. At lower pH γ decreases with time due to saturation of the surface layer. These effects demand careful attention to the design of experiments and the model used to interpret the results. The results cited in the table from different experimental systems, are however in reasonably good agreement, especially when the uncertainties and assumptions made are taken into account. Thus after correction for gas phase diffusion and exposure time, the values reported for the initial uptake coefficient at pH > 6, lie in the range 0.06 to 0.13. The preferred value for the accommodation coefficient which is based on the work of Worsnop et al, Jayne et al and Ponche et al., is $\alpha_b = 0.11$ with an uncertainty $\pm 20\%$.

Jayne et al investigated the time and pH dependence of γ in detail. They found that in the high pH range the uptake is governed by the rate of reaction of SO₂ with H₂O to form HSO₃⁻. In this case γ_i at fixed pH/exposure time is given by the following expression:

$$\Gamma_b = \frac{4H^*RT(D_l k^l)^{1/2}}{c} \quad (2)$$

where k^l is the pseudo first order rate constant for reaction of SO₂ with H₂O.

However if the value of k^l in bulk aqueous solution measured by Eigen and co-workers ($= 3.4 \times 10^6 \text{ s}^{-1}$; $(D_l/k^l)^{0.5} = 15 \text{ nm}$) is employed in eq.2, the predicted γ is substantially lower than the observed values. The discrepancy also extends to low pH when uptake is limited by Henry's law solubility. Jayne et al.(1990) suggest that this discrepancy in uptake rate could be due to a rapid surface reaction to form an HSO₃⁻ – H⁺ surface complex, which is in equilibrium with gas-phase SO₂. This complex allows a more rapid entry of S(IV) into the bulk as HSO₃⁻ compared to transfer and reaction of SO₂ molecules.

We interpret the surface complex as suggested by Jayne et al. as the adsorbed species as defined within the framework outlined in the guide to the heterogeneous data sheets; see also Ammann and Pöschl (2007) for a complete time dependent modelling of this uptake process. The equilibrium constant denoted by A^*_{eq} by Jayne et al. is equal to K_{LinC} used here; similarly, the kinetic parameters $k_{i-g}=k_{\text{des}}$ and $k_{i-l}=k_{\text{sb}}$. As discussed in detail by Jayne et al., it is difficult to constrain these parameters from the available data of the time dependence of the uptake coefficients. K_{LinC} was obtained from the slope of the time dependent uptake coefficient. Because the surface accommodation coefficient is not directly accessible and

$$K_{\text{LinC}} = \frac{\alpha_s \bar{c}}{4k_{\text{des}}}$$

only the ratio of α_s and k_{des} is constrained by the experiment at low SO₂ pressures. The bulk accommodation coefficient is linked to these parameters via

$$\alpha_b = \alpha_s (1 - \theta) \frac{k_{\text{sb}}}{k_{\text{sb}} + k_{\text{des}}}$$

where the surface coverage is given by $\theta = \frac{K_{\text{LangC}}[X]_g}{1 + K_{\text{LangC}}[X]_g}$, with $K_{\text{LangC}}=K_{\text{LinC}}/N_{\text{max}}$, which

leads to the pressure dependence of α_b .

In absence of an additional loss process of the surface complex at the surface itself, and assuming that transfer of SO₂ into the bulk is driven by solubility only for acidic conditions, the uptake coefficient (eq 25 in guide to heterogeneous reaction data sheets) simplifies to:

$$\frac{1}{\gamma} \approx \frac{1}{\alpha_s} + \frac{1}{\Gamma_{\text{sb}}} + \frac{1}{\Gamma_{\text{sol}}} = \frac{1}{\alpha_b} + \frac{1}{\Gamma_{\text{sol}}} = \frac{1 + K_{\text{LangC}}[X]_g}{\alpha_s} + \frac{1}{\Gamma_{\text{sol}}} = \frac{1}{\alpha_s} + \frac{\alpha_s \bar{c}}{4k_{\text{des}} N_{\text{max}}} [X]_g + \frac{1}{\Gamma_{\text{sol}}}$$

This is equivalent to the expression used by Jayne et al. to fit the time and pressure dependent data at low pH. We have adopted a value of α_s of 1, with a large uncertainty. Reducing α_s by a factor of 10 leads to adjustments of k_{sb} and k_{des} of similar magnitude. These parameters describe the experimental uptake coefficients observed over a range of pH and contact times in the droplet train experiments reasonably well. Specifically, they lead to a value of α_b of 0.11 at low SO₂ pressure, consistent also with the other experiments. The temperature dependence of α_b reported by Worsnop et al. was very weak within 260 to 292 K, possibly due to opposing trends

of k_{des} and k_{sb} . Due to the significant uncertainties in the driving variables, we refrain from providing temperature dependent expressions for them.

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