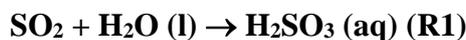


IUPAC Task Group on Atmospheric chemical Kinetic Data Evaluation – Data Sheet VI.A1.10 HET_H2OL_10

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Experimental data

Parameter	Temp./K	Reference	Technique/ Comments
γ , γ_0			
0.054±0.006 (init. droplet pH = 11.5)	295	Gardner et al., 1987, 1989	DT-TDL (a)
$\gamma_0 = 0.12$			
$\gamma_0 = 0.11±0.2$ (init. droplet pH = 11.5)	260-292	Worsnop et al., 1989	DT-TDL (b)
8.0×10^{-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 (pH = 13)	293.5	Shimono and Koda, 1996	(f)
7.7×10^{-3} (pH = 5.6)			
0.02 (pH = 4)	283	Boniface et al., 2000	DT-MS (g)
0.03 (pH = 7)	283		
0.05 (pH = 11)	283		
0.1 (pH = 12)	283		
0.16 (pH = 13)	283		
0.18 (pH = 14)	283		
0.05 (pH = 4)	264		
0.02 (pH = 4)	291		
0.08 (pH = 11)	264		
0.04 (pH = 11)	291		
0.34 (pH = 14)	264		
0.15 (pH = 14)	291		
<i>Accommodation coefficient, α_b</i>			
0.18	291	Boniface et al., 2000	DT-MS (g)
0.42	264		
<i>Rate coefficients, $k_2 \text{ M}^{-1} \text{ s}^{-1}$</i>			
$(1.1±0.2) \times 10^{10}$	291	Boniface et al., 2000	DT-MS (g)
$K_{\text{LinC}} / \text{cm}$			

Comments

- (a) Uptake of SO_2 into a fast moving train of water droplets (80 to 180 μm diam). $[\text{SO}_2]$ ((1.5 - 15.0) $\times 10^{12}$ molecule cm^{-3}) was measured by diode-laser adsorption. Surface saturation effects were shown to be absent at $[\text{SO}_2]$ and initial pH used. Measurements of aqueous $[\text{S(IV)}]$ in exposed droplets confirmed uptake coefficient values determined from SO_2 loss. Correction for gas phase diffusion to a static drop gives the cited value of γ_0 , which can be considered equal to the bulk accommodation coefficient.
- (b) Experiment designed to determine the temperature-dependent mass accommodation coefficients of SO_2 and H_2O_2 on aqueous surfaces, using oxidation of HSO_3^{2-} to overcome solubility limitation of S(IV) uptake. 200 mm diam. water droplets with $[\text{SO}_2]_0 = 1 \times 10^{13}$ 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 bulk 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 $[\text{SO}_2]_0$ of 10^{13} and 10^{15} molecule cm^{-3} . Corrections for gas phase diffusion and additional acidification of the droplet due to SO_2 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 SO_2 density (10^{13} molecule cm^{-3}). The observed uptake rates over the pH range were significantly greater than predicted on the basis of the known rate of SO_2 reaction in bulk liquid water at $\text{pH} > 5$ and known Henry solubility at low pH. A mechanism involving formation of a surface complex yielding $\text{HSO}_3^- + \text{H}^+$ was proposed. They derive kinetic and thermodynamic parameters governing these surface interactions.
- (d) Liquid jet of water (100 μm diameter); H_2O_2 was added in order to rapidly oxidize SO_2 (typically 100 ppm) to sulfate. The uptake kinetics of SO_2 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 $[\text{SO}_2]$ due to a change in surface pH. Addition of NH_3 to the SO_2/air mixture minimized the pH dependence.
- (e) Uptake into droplet train of $[\text{SO}_2] = 2.8$ to 28 ppmv. Dilute aqueous H_2O_2 was added to the condensed phase to rapidly oxidize dissolved SO_2 to H_2SO_4 . 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 $\text{pH} < 11$, on the interaction time. Cited value of γ_0 , which is independent of pH, is corrected for gas phase diffusion and represents the bulk accommodation coefficient. (The uncorrected γ_0 at $t = 0$ was 0.060 ± 0.008).
- (f) Uptake measurement of SO_2 on counterflowing liquid H_2O using LIF detection of SO_2 excited at 224.34 nm. The range of $[\text{SO}_2]$ was between 3.3×10^{11} and 1.7×10^{14} 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 SO_2 in the impinging flow field and was found to strongly depend on the pH of the condensed phase. The temperature dependence indicated an activation energy of -6 kJ mol^{-1} .
- (g) DT setup as in (c). Interaction times 2-15 ms; 150-300 μm droplet diameter; SO_2 concentrations 10^{13} - 10^{14} molecule cm^{-3} . The α_b and k_2 values listed in the table were obtained from a global fit to the measured pH and T dependent γ , including correction for the fact that the droplet surface region had an effectively lower pH than the bulk droplet during the short time scale of

the experiment. The T dependence of α_b yielded $\Delta H = -34 \pm 3 \text{ kJ mol}^{-1}$ and $\Delta S = -122 \pm 9 \text{ J mol}^{-1} \text{ K}^{-1}$ for the transition state.

- (h) Surface tension and second harmonic generation (SHG) experiments of sodium bisulfite solutions (0 – 3.6 mol kg⁻¹), in not completely closed system. [SO₂ (aq)]/[S(IV) (aq)] was estimated as 0.01 (based on dissociation equilibria and measured pH). SHG signal and surface excess derived from surface tension measurement fit with a Langmuir isotherm. Apparent Langmuir constant interpreted as equilibrium constant giving $\Delta G_{bs} = -14 \text{ kJ mole}^{-1}$ (bulk-surface), which was converted to $\Delta G_{gs} = -23 \text{ kJ mole}^{-1}$ using a Henry's law constant of 1.3 M atm⁻¹.

Preferred values

Parameter	Value	T/K
α_s	1	260 - 298
$k_{des} \text{ (s}^{-1}\text{)}$	$1 \times 10^{13} \exp(-6040/T)$	260 - 298
$k_{sb} \text{ (s}^{-1}\text{)}$	$5 \times 10^6 \exp(-2300/T)$	260 - 298
$N_{max} \text{ (cm}^{-2}\text{)}$	2.5×10^{14}	260 - 298
$K_{LinC} \text{ (cm)}$	0.5	298
$k_s \text{ (s}^{-1}\text{)}$	15.0	260 - 298
k_b^1 / s^{-1}	$3.4 \times 10^6 + 2.65 \times 10^{14} \times ((D_{OH} + D_{SO_2}) / (\text{cm}^2 \text{ s}^{-1})) \times ([OH^-] / M)$	260 - 298
<i>Reliability</i>		
$\Delta \log(\alpha_s) \text{ (s}^{-1}\text{)}$	1	260 - 298
$\Delta \log(k_{des}) \text{ (s}^{-1}\text{)}$	1	260 - 298
$\Delta \log(k_{sb}) \text{ (cm}^{-2}\text{)}$	1	260 - 298
$\Delta \log(k_s) \text{ (s}^{-1}\text{)}$	1	260 - 298
$\Delta \log(k_b^1) \text{ (cm}^{-2}\text{)}$	0.3	260 - 298
$\Delta \log(N_{max}) \text{ (cm)}$	0.3	260 - 298
$\Delta \log(K_{LinC}) \text{ (cm)}$	0.3	260 - 298

Comments on Preferred values

The uptake of SO₂ is a complex process involving a surface complex and pH dependent dissolution and dissociation, which is time dependent for large droplets. γ can be represented by

$$\frac{1}{\gamma} = \frac{1}{\alpha_s} + \frac{1}{\Gamma_s + \frac{1}{\frac{1}{\Gamma_{sb} + \frac{1}{\Gamma_{sol}(SO_2) + \frac{1}{\frac{1}{\Gamma_b + \Gamma_{sol}(HSO_3^-)}}}}}} \quad (1)$$

For interaction times sufficiently long (or particles small enough) to allow for solubility equilibration, the expression simplifies to:

$$\frac{1}{\gamma} = \frac{1}{\alpha_s} + \frac{1}{\Gamma_s + \frac{1}{\frac{1}{\Gamma_{sb} + \Gamma_b}}} \quad (2)$$

SO₂ enters the aqueous phase via formation of an adsorbed SO₂·H₂O complex, as apparent from surface tension measurements (Donaldson et al., 1995) and non-linear optical spectroscopy (Donaldson et al., 1995; Tarbuck and Richmond, 2006; Shamay et al., 2011; Ota et al., 2011), theory (Bishenden and Donaldson, 1998), and from kinetic data (Jayne et al., 1990).

In the absence of strong constraints, we recommend $\alpha_s = 1$. k_{des} is estimated from the pressure dependent experiments by Jayne et al. (1990) who estimated a binding energy of the complex of 12 kJ mol⁻¹ driving the activated desorption of SO₂ with the preferred rate expression given in the table. K_{LangC} can be obtained from

$$K_{LangC} = \frac{\alpha_s \bar{c}}{4k_d N_{max}} \quad (3)$$

The preferred value for N_{max} is the average of the value estimated by Jayne et al. (1990) and that reported by Donaldson et al. (1995) based on surface tension measurements. This leads to the rate limiting term for the surface reaction:

$$\Gamma_s = \frac{4K_{Lang}ck_sN_{max}}{\bar{c}(1+K_{Lang}c[SO_2]_g)} \quad (4)$$

Uptake at low pH is dominated by reaction on the surface, which is represented by a first-order process to convert the complex into HSO_3^- . The temperature independent, preferred value for k_s was obtained by adjusting γ to the temperature dependent data of Boniface et al. (2000) at low pH < 3 and the pressure dependent data by Jayne et al. (1990). Since the corrections for gas phase diffusion and for the time dependent acidification of the droplets are not well documented for the data in the figures of Jayne et al., consistency with the later data set by Boniface et al. by the same group for low pH was given priority. However, the parameter set given in the table gives a factor of 3 decrease in γ when $[SO_2]_g$ increases from 10^{13} to 10^{15} molecule cm^{-3} , qualitatively consistent with the observations by Jayne et al. (1990) and Shimono and Koda (1996). Overall, the values parameterizing the surface processes are somewhat different from those suggested by Jayne et al. (1990), but justified by the larger temperature range covered by Boniface et al. (2000) (same group, same technique) and the further information about the surface complex (surface tension and non-linear optical spectroscopy) mentioned above.

Transfer of $SO_2 \cdot H_2O$ into the bulk is given by:

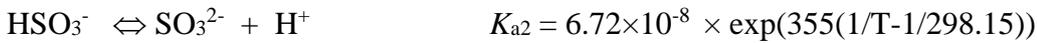
$$\Gamma_{sb} = \frac{\alpha_s k_{sb}}{k_d} \quad (5)$$

The preferred expression for k_{sb} was derived from fitting an Arrhenius expression to the temperature dependent value of the bulk accommodation coefficient,

$$\alpha_b = \frac{\alpha_s k_{sb}}{k_{sb} + k_d},$$

reported by Boniface et al (2000) from a global fit to their data. Boniface et al. (2000) used the temperature dependence of α_b to obtain $\Delta H = -34 \pm 3$ kJ mol^{-1} and $\Delta S = -122 \pm 9$ J mol^{-1} K^{-1} for the transition state.

When SO_2 enters aqueous solution it reacts with water molecules and an equilibrium is set up between the forms of S(IV): hydrated SO_2 , HSO_3^- and SO_3^{2-} via the following equilibria (Warneck and Williams, 2012):



where
$$H = \frac{[SO_2 \cdot H_2O]}{p(SO_2)}; K_1 = \frac{[H^+][HSO_3^-]}{[SO_2 \cdot H_2O]}; K_2 = \frac{[H^+][SO_3^{2-}]}{[HSO_3^-]}$$

which gives in turn:

$$[S(IV)]_{total} = p(SO_2) H \times \left\{ 1 + \frac{K_1}{[H^+]} + \frac{K_1 K_2}{[H^+]^2} \right\} = p(SO_2) H^* \quad (7)$$

H^+ from hydrolysis of SO_2 taken up to large, unbuffered droplets in laboratory experiments performed with high SO_2 concentrations over short time scales (as in droplet train experiments) leads to lower effective pH near the surface. Assuming that gas-phase SO_2 is in equilibrium with $SO_2(aq)$ near the liquid surface and neglecting the second dissociation involving K_2 , the actual $[H^+]$ at the surface is given by:

$$[H^+] = H' \pm \left(H'^2 + K_w + K_1 [SO_2] \right)^{1/2} \quad (8)$$

where

$$H^+ = \frac{1}{2} \left([\text{H}^+]_0 - \frac{K_w}{[\text{H}^+]_0} \right) \quad (9)$$

Data reported by Jayne et al. (1990), Shimono and Koda (1996) and Boniface et al. (2000) have been corrected for this effect by numerically solving for the ion balance.

The time-dependent resistance term for establishing solubility equilibrium in the droplet is given by (see Shi et al. (1999) for details of the integration of acid dissociation into the resistor model as shown in equation (1):

$$\Gamma_{sol}(\text{SO}_2) = \frac{4RTH}{\bar{c}} \left(\frac{D_{L,\text{SO}_2}}{t} \right)^{1/2} \quad \text{and} \quad \Gamma_{sol}(\text{HSO}_3^-) = \frac{4K_{a1}RTH}{\bar{c}} \left(\frac{D_{L,\text{HSO}_3^-}}{t} \right)^{1/2} \quad (10)$$

The diffusion coefficients can be obtained using the Stokes-Einstein relation:

$$D_{l,x} = \frac{k_B T}{6\pi\eta r_{d,x}}$$

Where the viscosity of water can be expressed as $\eta = 0.000024 \times 10^{(247.8/(T-140))}$ (Kestin et al., 1978) and the hydrodynamic radii for SO_2 , HSO_3^- and OH^- are estimated as 1.6×10^{-10} m, 1.8×10^{-10} m and 1.0×10^{-10} m.

The reactive dissolution of SO_2 can be described by:

$$\Gamma_b = \frac{4RTH \sqrt{D_l k_b^1}}{\bar{c}}$$

where k_b^1 is the pseudo first order rate constant for the reaction of SO_2 with H_2O . k_b^1 is given by $k_b^1 = k_1 + k_2[\text{OH}^-]$. k_1 in bulk aqueous solution was measured by Eigen et al. (1961) ($3.4 \times 10^6 \text{ s}^{-1}$). Boniface et al. (2000) found the value for k_2 at the diffusion limit ($(1.1 \pm 0.2) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ at 283 K), leading to the preferred expression for k_b^1 given in the table.

γ calculated using equation (1) reproduces the extensive pH and T dependent dataset of Boniface et al. (2000) (also considered an update of the Jayne et al. (1990) data) as well as that by Shimono and Koda (1996), and is also in good agreement with the single values reported by the other studies. Given the very different experimental technique used by Shimono and Koda (1996), which operated with longer interaction times (at the expense of sensitivity to gas phase diffusion), the agreement is very good. Shimono and Koda discuss the difference of about a factor of four at low pH in terms of the possibility that in droplet train experiments internal eddies may occur that effectively reduce the interaction time and thus lead to an apparent increase of γ due to the $(D_l t)^{-1/2}$ term in Γ_{sol} .

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