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## $SO_2$ + $H_2O_2$-doped ice

### Experimental data

| *Parameter* | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|
| *Experimental uptake coefficients:* $\gamma(SO_2)$ | | | |
| (0.7-5.3) x $10^{-4}$ (3.0 wt % $H_2O_2$-ice film) | 191 | Chu et al. 2000 | CWFT-MS (a) |
| ~8.3 x $10^{-5}$ (3.0 wt % $H_2O_2$-ice film) | 211 | | |
| (0.1-1.0) x $10^{-5}$ (0.8 wt % $H_2O_2$-ice film) | 191 | | |
| $\gamma(SO_2)$ = (0.9-9.0) x $10^{-3}$ for $P(SO_2)$ fixed at 1.5 x $10^{-6}$ mbar and $P(H_2O_2)$ = 2 x $10^{-5}$-2.5 x $10^{-4}$ mbar | 228 | Clegg and Abbatt, 2001 (b) | CWFT-MS (b) |
| $\gamma(SO_2)$ = (30 - 1.0) x $10^{-3}$ for $P(H_2O_2)$ fixed at 8.7 x $10^{-5}$ mbar and $P(SO_2)$ = (0.3 - 20) x $10^{-6}$ mbar | 228 | | |

### Comments

(a) $H_2O_2$ doped ice surfaces were prepared by bubbling helium through $H_2O_2$ solutions (30 wt % or 3 wt %) into a flow tube at 190-211 K via a sliding injector. The resulting vapour deposited ice films were determined to contain 3 wt % and 0.8 wt % $H_2O_2$, respectively. The average film thickness was estimated to be ~2.5 µm. The $SO_2$ partial pressure ranged from 1.6 x $10^{-5}$ to 5.1 x $10^{-5}$ mbar for uptake experiments on water-ice. The initial uptake coefficients, $\gamma_0$, were corrected for axial and laminar diffusion. Corrections for surface roughness were performed using a layered pore diffusion model; giving the "true" value for the uptake coefficient, $\gamma_t$, which are cited. These uptake coefficients decreased slightly with increasing $SO_2$ partial pressure at 191 K, and were constant at 211 K. The surface coverage of $SO_2$ on the 3.0 wt % $H_2O_2$ ice film ranged from 7 x $10^{13}$ to 4.7 x $10^{15}$ molecules/cm$^2$ as the temperature increased from 191 to 211 K at a constant $SO_2$ partial pressure of 1.7 x $10^{-6}$ mbar. It was shown by analysis of the exposed films by IC that $SO_2$ was converted to sulphate upon uptake into $H_2O_2$ -doped films.

(b) water-ice films were made by freezing a water-coated pyrex sleeve within the flow tube. Doped ice surfaces were prepared by flowing $H_2O_2$ over the ice film from the back of the flow tube until the entire length of the film surface was at equilibrium with the gaseous $H_2O_2$. A moveable sliding injector containing $SO_2$ was pulled back in stages over the ice film. The $SO_2$ and $H_2O_2$ partial pressure ranges are given in the table and in all cases, the $H_2O_2$ was the excess reagent. $SO_2$ uptake on $H_2O_2$-doped ice films was much larger than on pure ice and was irreversible. For a fixed $SO_2$ partial pressure of 1.5 x $10^{-6}$ mbar, the $SO_2$ reaction probability varied linearly with the $H_2O_2$ partial pressure up to 3 x $10^{-4}$ mbar. For a fixed $H_2O_2$ partial pressure of 8.7 x $10^{-5}$ mbar, the $SO_2$ reaction probability decreased with $p(SO_2)^{-0.7}$ in the range (0.27 to 17) x $10^{-5}$ mbar

## Preferred Values

| Parameter | Value | T/K |
|---|---|---|
| $k_s$ / cm$^2$ molecule$^{-1}$ s$^{-1}$ | 4 x $10^{-12}$ | 228 |
| $k_s K_{linC}(SO_2)$ /cm$^3$molecule$^{-1}$ s$^{-1}$ | 2.9 x $10^{-15}$exp(2065/T) | 200- 230 |
| $K_{linC}(H_2O_2)$ /cm | 1.6 | 228 |
| $N_{max}$ / molecule cm$^{-2}$ | 3 x $10^{14}$ | |
| *Reliability* | | |
| $\Delta \log (k_s K_{linC}(SO_2))$ | ± 0.3 | 228 |
| $\Delta$ (E/R) /K | ± 1000 | 200-298 |

*Comments on preferred values*

Both Chu et al. (2000) and Clegg and Abbatt (2001) observed that the $SO_2$ uptake is significantly enhanced by the presence of adsorbed $H_2O_2$. Unlike the reversible $SO_2$ uptake observed on pure water-ice, the uptake on $H_2O_2$-doped ice is irreversible. This is due to the reaction of between $H_2O_2$ and $SO_2$ forming sulfates on the ice surface (Chu et al., 2000). However $SO_2$ loss rate was still time-dependent, declining as the surface was exposed. This was attributed to accumulation of $H_2SO_4$ products on the ice surface, which inhibits $SO_2$ uptake. (see $SO_2$ + ice data sheet, IUPAC 2009). This is as observed in some of the Chu et al. (2000) experiments, but the dependence of $\gamma$ on the $SO_2$ partial pressure is stronger and better defined in the experiments of Clegg and Abbatt (2001). Note that a direct comparison between the experimental results of Chu et al. (2000) and those of Clegg and Abbatt (2001) is difficult as $H_2O_2$ surface coverages were uncertain in the experiments of Chu et al. (2000) who used frozen solutions of $H_2O_2$.

Clegg and Abbatt (2001) suggested the following mechanism to explain their observations:

$$H_2O_2\,(g) \leftrightarrow H_2O_2\,(ads) \quad (1)$$
$$SO_2\,(g) \leftrightarrow SO_2\,(ads) \quad (2)$$
$$SO_2\,(ads) + H_2O \leftrightarrow H^+(ads) + HSO_3^-(ads) \quad (3)$$
$$HSO_3^-(ads) + H_2O_2\,(ads) \rightarrow HOOSO_2^-\,(ads) + H_2O \quad (4)$$
$$HOOSO_2^-\,(ads) + H^+(ads) \rightarrow 2\,H^+(ads) + SO_4^{2-}(ads) \quad (5)$$

Eqn (4) is considered to be the rate-determining step. The overall rate of reaction is then proportional to $P_{SO_2}^{0.5} . P_{H_2O_2}$ , noting the square root dependence of the $SO_2$ surface coverage on the $SO_2$ partial pressure (see $SO_2$ + ice data sheet, IUPAC 2007), and the linear dependence on $H_2O_2$ coverage at low $P_{H_2O_2}$ . In terms of the reaction probability for $SO_2$, $\gamma(SO_2) \propto \Pi_{SO_2}^{0.5}$ . $P_{H_2O_2}$ .

However at low [$SO_2$], surface coverage of $SO_2$ on ice was approximately proportional to $P_{SO_2}$ , although the $SO_2$ reaction probability decreased with $p(SO_2)^{\sim 0.7}$ at fixed $H_2O_2$ coverage, indicating complexity in the chemistry. For this evaluation we adopt a simple Langmuir-Hinshelwood formalism, with the uptake coefficient $\gamma_{LH}$ given by:

$$\gamma_{LH} = \frac{4k_s[H_2O_2]_s K_{LinC}(SO_2)}{\bar{c}} \quad \text{with} \quad [H_2O_2]_S = N_{\max}\frac{K_{LangC}(H_2O_2)[H_2O_2]}{1+K_{LangC}(H_2O_2)[H_2O_2]}$$

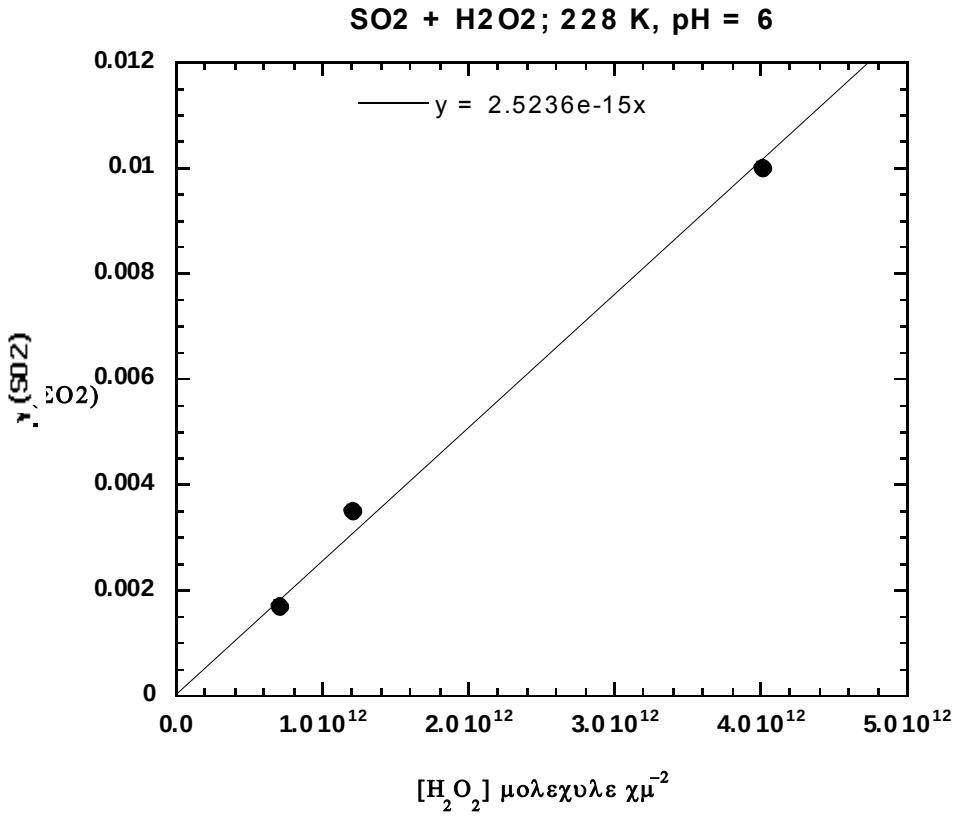
An average value for the parameter $k_s$ = 4 x $10^{-12}$ $cm^2molecule^{-1}s^{-1}$ at 288 K was evaluated from the experimental $[H_2O_2]$ dependence of $\gamma$ measured by Clegg and Abbatt (2001) on neutral (pH =6) ice, together with the IUPAC recommended value of $K_{LinC}(SO_2)$ (see $SO_2$ + ice data sheet, IUPAC 2009). This forms the basis of our recommendation, which should be applied only for $SO_2$ partial pressures below ~1 x $10^{-6}$ mbar. At higher $SO_2$ the following $[SO_2]$ dependent expression for $\gamma_{LH}$ gives a better description of the uptake rates:

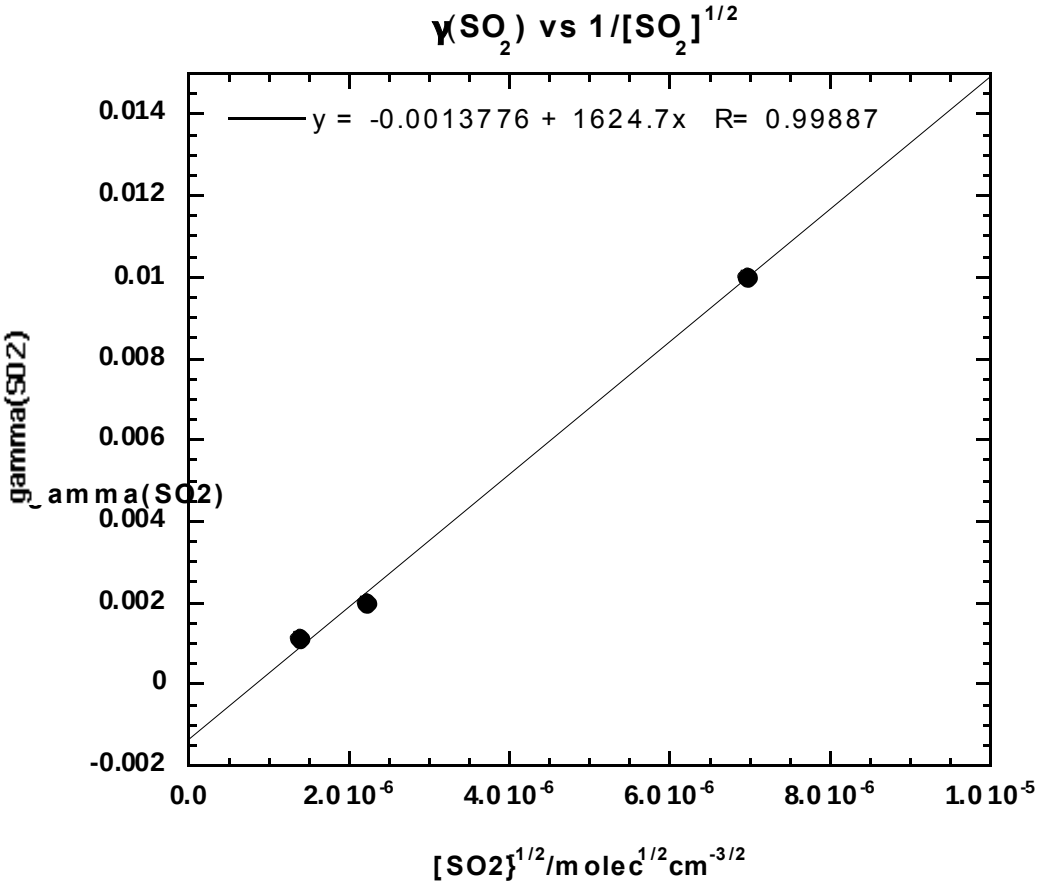
$$\gamma_{LH} = \frac{4k_s[H_2O_2]_s K(SO_2)}{\bar{c}\left([SO_2]_g^{0.5}\right)}$$ where $K(SO_2)$ is given in the $SO_2$+ice data sheet ( IUPAC 2009)

The strong influence of pH suggests that as $H_2SO_4$ builds up with each exposure of $SO_2$ to the $H_2O_2$-doped surfaces, the surface protons inhibit reaction 3, the dissociation of $SO_2$. This leads to less gas-phase $SO_2$ adsorbing to the ice surface and hence a lower reaction probability. Clegg and Abbatt (2001) estimate that about $10^{14}$-$10^{15}$ molecules/$cm^2$ (i.e approx 1 ML) of $H_2SO_4$ need to be formed before the $SO_2$ + $H_2O_2$ → $H_2SO_4$ reaction shuts off (i.e., before the surface becomes poisoned with protons).

## References


Chu, L., Diao, G. and Chu, L.T.: J. Phys. Chem. A 104, 7565 (2000).
Clegg, S. M and Abbatt, J. P. D.: Atmos Chem. Phys. 1, 73 (2001).
SO2 + ice datasheet, IUPAC 2007


SO2 + H2O2; 228 K, pH = 6
y = 2.5236e-15x
0.012
0.01
0.008
0.006
0.004
0.002
0
0.0
1.0 10^12
2.0 10^12
3.0 10^12
4.0 10^12
5.0 10^12
[H2O2] μολεχυλε χμ^-2


γ(SO2) vs 1/[SO2]1/2
y = -0.0013776 + 1624.7x R= 0.99887
gamma(SO2)
0.014
0.012
0.01
0.008
0.006
0.004
0.002
0
-0.002
0.0
2.0 10-6
4.0 10-6
6.0 10-6
8.0 10-6
1.0 10-5
[SO2]1/2/molec1/2cm-3/2