

Oxidation of sulphur dioxide in water droplets in the presence of ammonia

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Summary. — SO_2 oxidation by oxygen in monodisperse water droplets was studied in a cylindrical chamber, without and in the presence of ammonia. The range of SO_2 concentration was from about 10^{-2} to 5 ppmv, while the NH_3 input concentration was kept constant at about 4.7×10^{-2} ppmv. The contact time between gases and droplets was 210 s. The experimental results were compared with the theoretical values predicted by the kinetics of Larson *et al.* (*Atmos. Environ.*, **12** (1978) 1597) and McKay (*Atmos. Environ.*, **5** (1971) 7). Much higher sulphate concentrations were obtained in experiments run in the presence of NH_3 , as opposed to those without NH_3 . The experimental results agree with the values predicted by McKay's kinetics and are higher than Larson's.

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1. - Introduction

Sulphur dioxide, emitted from various sources such as fossil fuel combustion, the gas-phase of biogenic dimethylsulfides and vulcanic activity, can be oxidized in the atmosphere by homogeneous gas-phase reactions or heterogeneous processes, taking place either on the surface of solid particles or inside water (cloud or fog) by means of dissolved O_2 , O_3 or H_2O_2 . Trace substances frequently act as catalysts (Fe^{3+} , Mn^{2+} , soot, etc.). The latter oxidation reactions are pH sensitive because the reaction rates are influenced by $[\text{H}^+]$ or because the pH changes the solubility of SO_2 .

Sulphur dioxide oxidation can also be influenced by the presence of other gases, such as ammonia. For example, dry deposition of SO_2 on vegetation is enhanced in the presence of NH_3 and with increasing air humidity [1].

The role of NH_3 in SO_2 oxidation in an aqueous phase has been investigated in the past by many scientists [2-5]. Junge and Ryan [6], in a pioneering paper on SO_2 oxidation in a liquid phase, measured a much larger amount of SO_4^{2-} in the presence of

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NH_3 and were the first to observe the formation of ammonium sulphate in a much shorter time than was expected from experiments in which bulk solutions of the same type were mixed together, indicating that the rate of oxidation can be limited by the mass-transport of gases.

Easter and Hobbs [7] studied the SO_2 - NH_3 -liquid H_2O system and calculated the production of ammonium sulfate by the oxidation of dissolved sulphur dioxide in cloud droplets in a wave cloud situation, following the Scott and Hobbs [3] oxidation rate. The results show that significant increases in the concentration of active CCN at 0.5% supersaturation can be produced in the oxidation of SO_2 by the dissolved oxygen in cloud droplets in a short time (4 min) and with concentrations of SO_2 and NH_3 typical of unpolluted air (1 and 3 ppb, respectively).

Field experiments also emphasize the importance of NH_3 in the SO_2 oxidation process. In a series of measurements in orographic clouds at Great Dun Fell (England), designed to investigate the oxidation of SO_2 by means of H_2O_2 and O_3 , Clark *et al.* [8] demonstrated the importance of the presence of NH_3 , since the O_3 reaction is pH dependent and the ammonia concentration has an important influence on the pH of cloud water. The extrapolation of the results using a model demonstrates that, over a wide range of SO_2 concentrations, the total sulphate produced in the cloud is virtually independent of the initial SO_2 concentration and roughly proportional to the environmental ammonia concentration.

It is important to assess the rate at which SO_2 oxidation due to O_2 may occur in the atmosphere, since the fastest rate observed in the laboratory [9] would make the process very important especially in the presence of NH_3 , when compared with oxidation produced by other oxidisers in the atmosphere, while the lowest rate for the same process [10] suggests that it is of little consequence.

To increase our knowledge of the influence of ammonia in the oxidation process of SO_2 , we carried out laboratory experiments, using monodispersed droplets. These were used instead of polydispersed droplets, since the gas and liquid mass-transfer coefficients depend on the radius of the droplets. Using the latter, the SO_2 oxidation rate could have depended on the droplet size distribution.

2. - Experimental

The experimental techniques used in these experiments have already been presented in detail in [11]. A stream of air is passed through a Collison generator, which atomizes a dilute NaCl aqueous solution, thus producing condensation nuclei. The gas flow at the outlet is partly sent to a thermostated bath, where the water is vaporized at $T = 80^\circ\text{C}$. The droplets formed on condensation nuclei are vaporized and a controlled recondensation produces a cloud of monodispersed droplets. The droplet characterization technique employed a glass slide coated with black carbon and thermophoretic enhancement of droplet deposition by cooling the slide. The ratio of the droplet to spot diameter is 0.86. The droplet radius was $R = (2.0 \pm 0.3) \mu\text{m}$.

At the generator outlet the droplets enter a reaction chamber together with a mixture of SO_2 and NH_3 . Air, SO_2 and NH_3 are supplied by compressed-gas cylinders and their flow-rate ratio is varied to obtain variable concentration. The total flow was $(325 \pm 5) \text{ l h}^{-1}$. The chamber employed consists of a pipe measuring 200 cm in length and 11 cm in diameter and was heated slightly on the outside to prevent condensation on the inside surface. The contact time is 210 s. At the outlet of the pipe, the droplets

are captured on a specifically designed, circular trough impactor with a near unitary capture efficiency. The experiment lasts about 30 min. The gas stream at the outlet of the impactor is sucked for about 15' through a bubbler containing 40 cc of a 5% H_2O_2 and afterwards, for the same time period, through 40 cc of 0.1 N H_2SO_4 to measure the SO_2 and NH_3 concentrations in the gas.

The chemical analyses of SO_4^{2-} , NH_4^+ and Cl^- are performed with a Dionex ion chromatograph. Liquid water content (LWC), determined by the ratio between the water mass collected during each run and the flowed gas volume was $(3.8 \pm 0.1) \text{ g m}^{-3}$.

3. - Theoretical and experimental results

The experiments are made using monodispersed droplets grown on NaCl condensation nuclei at $T = (25 \pm 1) \text{ }^\circ\text{C}$. Cl^- concentration in the droplets is $(4.3 \pm 2.2) \text{ ppm}$.

The experimental data are reported in figs. 1 and 2. For comparison we report data obtained from the kinetics proposed by McKay [12], deduced from measurements of Fuller and Crist [9], and Larson *et al.* [13], for SO_2 oxidation due to oxygen in the presence of ammonia and in the absence of a catalyst. These researchers suggest that

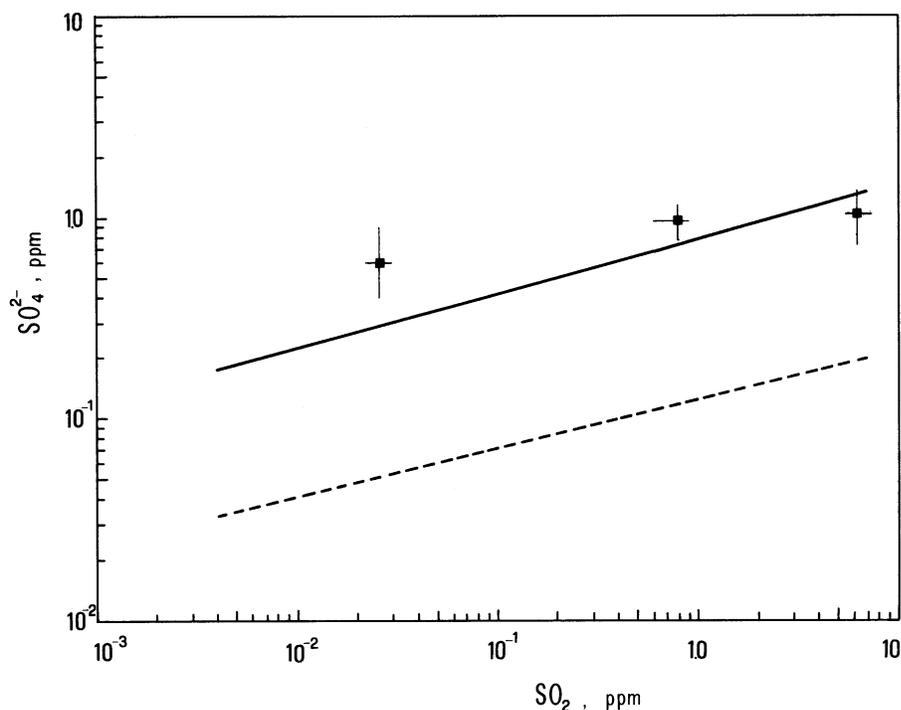


Fig. 1. - Sulphate concentration in the liquid phase as a function of SO_2 concentration in the gas phase, in the absence of NH_3 . Solid line, McKay's oxidation rate; dashed line, Larson's *et al.* oxidation rate. Squares represent average of three to five runs and bars indicate standard deviation.

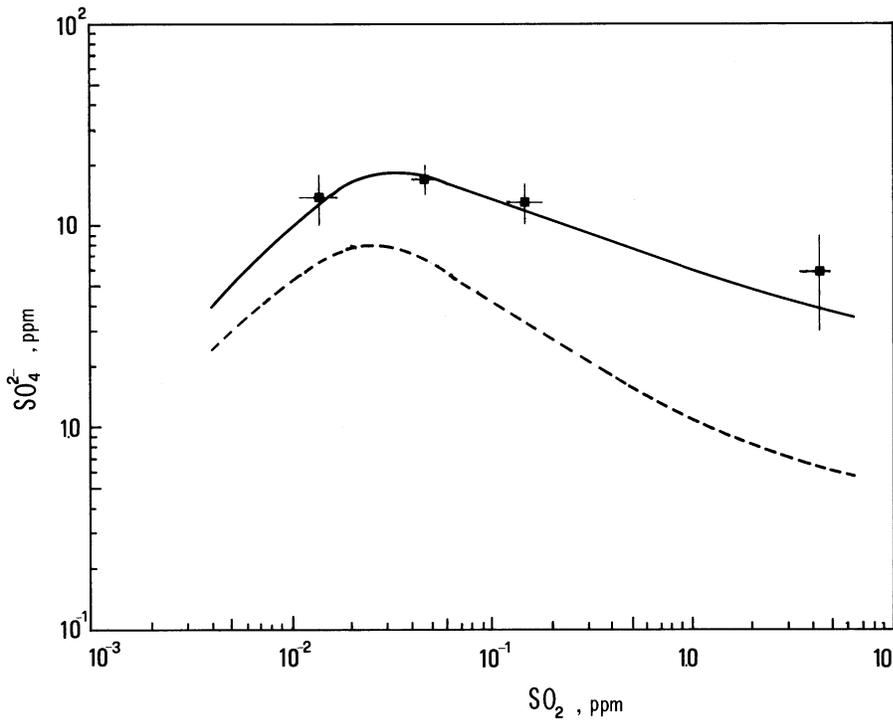


Fig. 2. - Sulphate concentration in the liquid phase as a function of SO_2 concentration in the gas phase, in the presence of NH_3 . Solid line, McKay's oxidation rate; dashed line, Larson's *et al.* oxidation rate. Squares represent average of three to five runs and bars indicate standard deviation.

the rate of production of SO_4^{2-} is given by the first-order rate equation

$$(1) \quad d[\text{SO}_4^{2-}]/dt = k[\text{SO}_3^{2-}].$$

The rate constants proposed by McKay [12] and Larson *et al.* [13] at $T = 298 \text{ K}$ are, respectively,

$$k_1 = 0.013 + 59 [\text{H}^+]^{0.5} \text{ s}^{-1}, \quad k_2 = 4.8 \cdot 10^{-3} + 8.9 [\text{H}^+]^{0.5} + 3.9 \cdot 10^{-12} \rho_{\text{O}_2} [\text{H}^+]^{-1} \text{ s}^{-1},$$

where $\rho_{\text{O}_2} = 0.2 \text{ atm}$ is the partial pressure of oxygen in the gas, $[\text{H}^+]$ is the concentration of hydrogen ion in the liquid phase, M. We choose these rate constants for comparison with the experimental data, as McKay's kinetics give a higher conversion rate with respect to all the values proposed [3, 10, 14, 15], while Larson *et al.* [13] give lower values than McKay's oxidation rate by almost one order of magnitude.

Chemical equilibrium equations, equilibrium constant expressions and values are given in table I.

By considering also the electroneutrality equation,

$$[\text{H}^+] + [\text{NH}_4^+] = [\text{OH}^-] + [\text{HSO}_3^-] + 2[\text{SO}_3^{2-}] + 2[\text{SO}_4^{2-}],$$

TABLE I. – *Reactions and equilibrium constants* (from Seinfeld [16]).

Chemical equilibrium equation	Equilibrium constant expression	Value of the equilibrium constant at $T = 298$ K
$\text{H}_2\text{O} = \text{H}^+ + \text{OH}^-$	$K_w = [\text{H}^+][\text{OH}^-]$	$1.008 \times 10^{-14} \text{ M}^2$
$(\text{SO}_2)_{\text{gas}} + \text{H}_2\text{O} = \text{SO}_2 \cdot \text{H}_2\text{O}$	$K_{\text{hs}} = [\text{SO}_2 \cdot \text{H}_2\text{O}] / \rho_{\text{SO}_2}$	1.24 M atm^{-1}
$\text{SO}_2 \cdot \text{H}_2\text{O} = \text{H}^+ + \text{HSO}_3^-$	$K_{\text{s1}} = [\text{H}^+] + [\text{HSO}_3^-] / [\text{SO}_2 \cdot \text{H}_2\text{O}]$	$1.29 \times 10^{-2} \text{ M}$
$\text{HSO}_3^- = \text{H}^+ + \text{SO}_3^{2-}$	$K_{\text{s2}} = [\text{H}^+][\text{SO}_3^{2-}] / [\text{HSO}_3^-]$	$6.014 \times 10^{-8} \text{ M}$
$(\text{NH}_3)_{\text{gas}} + \text{H}_2\text{O} = \text{NH}_3 \cdot \text{H}_2\text{O}$	$K_{\text{ha}} = [\text{NH}_3 \cdot \text{H}_2\text{O}]$	62 M atm^{-1}
$\text{NH}_3 \cdot \text{H}_2\text{O} = \text{NH}_4^+ + \text{OH}^-$	$K_{\text{a1}} = [\text{NH}_4^+][\text{OH}^-] / [\text{NH}_3 \cdot \text{H}_2\text{O}]$	$1.709 \times 10^{-5} \text{ M}$

we obtain the following equation:

$$\text{H}^3 (1 + K_{\text{ha}} K_{\text{a1}} / K_w) \rho_{\text{NH}_3} - 2\text{H}^2 [\text{SO}_4^{2-}] - \text{H} (K_w + K_{\text{hs}} K_{\text{s1}} \rho_{\text{SO}_2}) - 2 K_{\text{sh}} K_{\text{s1}} K_{\text{s2}} \rho_{\text{SO}_2} = 0.$$

In our calculations (at $T = 298$ K) we suppose a constant LWC and an instantaneous equilibrium between the gas and the liquid phase for each gas considered (O_2 , SO_2 , NH_3). Therefore diffusion is not considered to be a controlling factor, either in the gas or the liquid phase and the only chemical step is the sulphate oxidation. From input SO_2 , NH_3 gas-phase concentration and LWC, an iterative program calculates the aqueous and the residual gas-phase concentrations that result when the SO_2 and NH_3 are dissolved in liquid water. The equilibrium between the two phases produces a depletion of NH_3 and SO_2 in the gas phase. While for input $\text{SO}_2 > 0.5$ ppmv depletion in the gas phase is small and decreases with increasing SO_2 concentration, for NH_3 it is always appreciable with respect to the initial concentration. For example, with $\text{LWC} = 3.8 \text{ g m}^{-3}$, $\text{NH}_3 = 0.047$ ppmv and $\text{SO}_2 = 0.5$ ppmv, the equilibrium value for NH_3 and SO_2 are, respectively, 0.34 ppbv and 0.452 ppmv. So, at equilibrium, we have ammonia gas-concentrations comparable with those present in the atmosphere.

We do not consider the CO_2 equilibrium, since in our experiment the water used to produce monodisperse droplets is at $t \cong 80$ °C, so it contains no dissolved CO_2 .

The initial rate of production of SO_4^{2-} is given by (1). Sulphate production changes H^+ , NH_4^+ , and SO_3^{2-} concentration in the liquid phase and NH_3 and SO_2 equilibrium concentrations in the gas phase.

Therefore, we can calculate sulphate production with an iterative procedure after the contact time $t = 210$ s used in our experiments, to compare the theoretical data with those obtained experimentally. The input NH_3 concentration (before transfer of NH_3 from a liquid to a gas phase) is (0.047 ± 0.03) ppmv. Input NH_3 (as for SO_2) concentrations were measured from NH_4^+ (SO_4^{2-}) measured in the captured droplets and from NH_3 (SO_2) measured in the gaseous phase, at the outlet of the column.

In fig. 1 we also report sulphate production due to the oxidation of O_2 , in the absence of ammonia, following the same kinetics, and experimental results.

4. – Discussion

From fig. 1 we can observe that sulphate concentration in a liquid phase, produced after 210 s, following McKay and Larson's kinetics, increases slowly with increasing SO_2 gas concentration in the absence of ammonia. This depends on the fact that Larson and McKay's kinetics suppose that the SO_3^{2-} ion is oxidized and the theoretical equilibrium shows that SO_3^{2-} concentration changes are small in relation to the SO_2 concentration.

For SO_2 concentrations comparable with the atmospheric values, the calculations show a sharp increase in sulphate production in the presence of ammonia ($\text{NH}_3 = 0.047$ ppm), compared to when it is absent. Sulphate concentration shows a maximum when SO_2 and NH_3 input concentrations are comparable (fig. 2). In fact, ammonia can buffer the solution pH, so there is an increase of SO_3^{2-} . A further increase of SO_2 concentration can reduce sulphate production due to the limited buffering capacity of the ammonia. That is, while an increase of ammonia concentration should theoretically always produce an increase in sulphate production, this is not the case for SO_2 .

By examining our laboratory results, we observe that experimental data can be explained by supposing that the SO_3^{2-} ion is oxidized, following McKay's kinetics and in absence of diffusive resistance. In fact, following Freiberg and Schwartz [17] and considering the droplet radius and gas concentrations used in our experiments, the characteristic time for the gas ($\tau_{d,g}$) and the liquid-phase diffusion ($\tau_{d,a}$) are much lower than the characteristic time associated with the oxidation reaction in the liquid phase, relative to the gas-phase SO_2 concentration ($\tau_{c,g}$) or to aqueous sulphur-IV species ($\tau_{c,a}$), respectively. For example $\tau_{d,g}$ is about 10^{-8} s for all gases considered (O_2 , SO_2 , NH_3) and $\tau_{d,a} \cong 10^{-4}$ s in liquid phase. If we consider for example an input SO_2 and NH_3 gas-phase concentration of 2×10^{-2} and 4.7×10^{-2} ppmv, respectively, following McKay's kinetics, the $\tau_{c,a}$ will range from 60 to 120 s (during a 210 s period of time) and $\tau_{c,g}$ will range from 2×10^{-5} to 10^{-4} s. In addition, with the same SO_2 and NH_3 concentrations, the characteristic time (t_{reag}) required for gas-phase diffusion to supply an amount of reagent (SO_2) to the droplet necessary to produce a concentration of dissolved reagent in equilibrium with its concentration in the bulk gas-phase, is about 0.5 s (in the absence of NH_3 it would be about 10^{-3} s) which is much lower than the experimental duration (210 s). Characteristic times of the aqueous dissociation reactions of SO_2 are very short when compared with the others. Consequently, we must consider the several aqueous sulphur-IV species to be in equilibrium.

A discrepancy exists in the available literature on the aqueous oxidation of SO_2 by oxygen. Many researchers [3, 15, 18] agree that the uncatalyzed oxidation of SO_2 in aqueous systems occurs by a first-order reaction in SO_3^{2-} and no oxidation of HSO_3^- occurs directly, but the rate constants proposed are very different. For example, at $\text{pH} = 6$ and $T = 298$ K, Fuller and Crist give $k \approx 7 \times 10^{-1} \text{ s}^{-1}$, while Brimblecombe and Spedding $6 \times 10^{-3} \text{ s}^{-1}$. Thus disparity may be due to impurity in either the reagent or the water or to mass-transport limitation (in the gas and/or aqueous phase). Following Dasgupta [19], probably the rate observations most easily reproduced were made by Fuller and Crist.

Some researchers propose further kinetics. Hansen *et al.* [20] studied the SO_2 oxidation in the presence of NH_3 in laboratory clouds, by using NaCl and soot particles as cloud condensation. The rate of SO_4^{2-} formation was observed to be as much as two orders of magnitude greater than that predicted by Larson's equation. According to these researchers sulphate formation is essentially independent of the type of nuclei on which the cloud forms.

Benner *et al.* [21], in a laboratory experiment in a thin water film, found that the oxidation rate exceeded the rate expression of Larson *et al.* by about one order of magnitude, *i.e.* a smaller enhancement with respect to that observed in the previously reported droplet reaction. Hansen *et al.* and Benner *et al.* interpreted their findings in terms of the enhanced adsorption of the reacting gases on the droplet surface, as reported by Jayne *et al.* [22]. These authors suggest that at the gas-liquid interface, gaseous SO_2 collides with a water molecule and forms the surface complex $\text{HSO}_3^- \cdot \text{H}^+$ (chemisorption process) which is in equilibrium with the gas-phase SO_2 . Such an intermediate surface complex may then enter the bulk-liquid as HSO_3^- .

Adema and Heeres [23] in a study on the dry deposition of SO_2 in air on a thin water layer (4–4600 μm), in the presence of ammonia, concluded that the oxidation of HSO_3^- occurs at the surface of the water and that the results cannot be explained by the oxidation of the SO_3^{2-} ion.

As regards Hansen's results, there is important evidence that cloud formation occurs in the presence of reactive gases, so initially there were much high concentrations of catalyzers (Cl^- and soot) in the droplets, that can influence the oxidation process. This condition could at least partially explain the high sulphate conversion obtained. Moreover, Jayne *et al.* [22], by studying the effects of the H_2O_2 content on the uptake of SO_2 by aqueous droplets, concluded that there is no measurable reaction of H_2O_2 with surface chemisorbed SO_2 , *i.e.* the bulk reaction kinetics of H_2O_2 with dissolved S(IV) dominate the reactive uptake. Thus, even supposing the formation of a surface-complex, this would not necessarily produce an increase in the oxidation of SO_2 in liquid droplets. In conclusion, according to our experimental data, the oxidation of SO_2 in cloud droplets, with or without ammonia, could be explained by McKay's kinetics, with no need to introduce the assumptions made by the researchers quoted above.

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