An Experimental Test of a Theoretical Model to Determine the Rate at which Freely Falling Water Drops Scavenge SO_2 in Air

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ABSTRACT

An experimental method involving the UCLA Rain Shaft is described. This method allows determining the rate at which SO_2 is scavenged from air by freely falling water drops. In the present experiment water drops of radii near 300 μm were allowed to pass through a chamber filled with SO_2 whose partial pressure was determined by an infrared spectrometer. By varying the length of the gas compartment, the drops could be exposed to SO_2 for different intervals of time. An electrochemical method verified by three quantitative chemical methods was used to determine the total amount of sulfur taken up by the drops falling through the gas compartment. The present experimental results were compared with the results from our theoretical model (Baboolal *et al.*, 1981), which was evaluated for the present experimental conditions. Satisfactory agreement between experiment and theory was found.

1. Introduction

Recent studies show that wet-deposition involving clouds and precipitation contributes significantly to the scavenging of air pollutants from the atmosphere. The field studies, carried out on this topic, and their limitations have been discussed by Baboolal *et al.* (1981) who also discussed some of the theoretical methods for solving the problem of gas scavenging by water drops in air.

Experimental methods, on the other hand, have a number of serious drawbacks, the major one being that experiments are usually restricted to sea level pressure and a narrow range of temperature and humidity conditions, while scavenging of pollutants in the atmosphere proceeds at all levels within the troposphere, and at a wide range of temperatures and humidities. In addition, it appears that individual experiments suffer considerably from a lack of realism with which actual cloud and precipitation drops were simulated.

Thus, Beilke and Georgii (1968) and Beilke[1] determined the half-life and the washout rate of SO_2, NO_2 and CO_2 in air, using water sprays for studying the washout of these gases in a chamber. Three spray nozzles were used, producing drops of 850, 400 and 150 μm mean radius. No precaution was taken to prevent the spray drops from becoming electrically charged. In addition, the drop size distribution produced were rather unrealistic in relation to those found in atmospheric clouds. However, the most serious drawback of these spray experiments stems from the fact that the water sprayed was recirculated, i.e., the spray drops, after having been passed through the gas chamber, were collected at the bottom of the chamber and the resulting liquid returned to the spray nozzel to form new drops, and so on. In this way, individual drops were allowed to scavenge in the chamber only for a short period of time after which they lost their identification upon being collected. Since the amount of gas scavenged by a drop is a function of the amount of SO_2 previously scavenged by the drop, it follows that the rate at which SO_2 is scavenged by drops that keep their identity over the whole scavenging period is considerably different from the rate at which SO_2 is scavenged by drops collecting periodically and reformed from the resulting liquid of the collected drops.

In another set of experiments, Barrie *et al.*[2] and Barrie and Georgii (1976) studied the absorption of SO_2 by single drops containing various catalyzing agents in them. Unfortunately the drops investigated were of 2 mm diameter only, and were suspended from a fixed support at the plastic tip of a glass capillary, rather than being allowed to fall freely at their terminal velocity in air. It is known that rigid methods of suspension distort the drop shape as well as the air flow around it, and the circulation

[1] Beilke, S., 1970: Laboratory investigations on washout trace gases. *Precipitations Scavenging—1970*, 261–269 [NTIS CONF-700601.]

[2] Barrie, L. A., S. Beilke, and H. W. Georgii, 1974: SO_2 removal by cloud and fog drops as affected by ammonia and heavy metals. *Precipitation Scavenging—1974*, 151–166 [NTIS CONF-741003.]

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within the drops. Since all these factors control the convective diffusion of SO_2 into drops, altering these factors will result in an unrealistic SO_2 uptake by drops.

In order to eliminate the deficiencies of previous experiments we have begin a new series of experiments.

2. Experimental set-up

The experiments described in the present article were carried out in the UCLA Rain Shaft. This concrete shaft extends over nine floors of the Mathematical Sciences Building at UCLA. It measures ~33 m in height and has a cross section of ~1 m^2. Two experimental set-ups were mounted in the concrete shaft: a *long tunnel* for studying large water drops 500–2500 μm in radius and a *short tunnel* ideal for studying small water drops of radii between 50 and 500 μm. The tunnels, although different in size, consisted of three main sections: an acceleration tube at the top, where the drops were generated and allowed to fall and reach terminal velocity; a gas compartment, where a gas of desired type and partial pressure could be housed for studying the rate at which it is removed by water drops falling through it, and finally, a bottom tube that contained Freon-12, an inert water insoluble gas. This final section acted as a short neutral zone between the gas compartment and the collector which was attached to the bottom of the Freon tube.

All the sections of the tunnel were made from plexiglas cylindrical tubes that had the following dimensions: for the *long tunnel*, the acceleration tube extended over 22 m and had a diameter of 0.46 m. The gas compartment was 10 m long and had a diameter of 0.15 m. The Freon tube was 0.6 m long and had a diameter of 0.15 m. The *short tunnel* consisted of an acceleration tube which was 7.6 m long and 0.15 m in diameter. Two interchangeable gas compartments, one 1.525 m long and the other 0.420 m long were used, both having a diameter of 0.76 m. The Freon tube was 0.65 m long and 0.76 m in diameter. The air in the shaft was purified and set at a desired humidity by circulation through filters. For the long tunnel, the temperature of the air at the top and at the bottom could be controlled independently, and to avoid convective disturbances in the tube, the air at the bottom was set at a temperature 2°C colder than at the top. The gas compartment had two gas-tight gates located at the top and at the bottom of that section. These could be sealed or opened for short time intervals to allow the drops to fall through. The length of the acceleration tube was chosen to ensure that the drops did reach terminal velocity at or before they reached the upper gate of the gas compartment. The distance needed for a drop to reach terminal velocity has been established both theoretically and experimentally by Wang and Pruppacher (1977).

The drops used were formed from doubly distilled and deionized water. The large water drops were generated using a technique involving hypodermic needles and a constant water head. The small water drops were formed using a drop generator of the type developed by Abbot and Cannon (1972). In each experiment, about 150 drops were allowed to pass in succession through the gas compartment. The drops were sized under the microscope catching them in a layer of oil just before they hit the collector at the bottom of the tunnel. The temperature and humidity of the air in the plexiglass tube system varied somewhat from day to day, the air always being below water saturation. Due to the large fall-speed of the drops, the water subsaturations did not cause a significant change in drop size during the fall of the drop. On the other hand, a lack of water saturation did cause the drops to assume a temperature lower than air temperature. The actual drop temperature was computed by a method described by Beard and Pruppacher (1971).

In the present article, we shall report on our scavenging studies of SO_2 by 300 ($\pm$20) μm radius drops. For this purpose the smaller of the two gas compartments was filled with high purity SO_2 (99.9% Liquid Carbonic, Los Angeles, CA). The amount of gas in the gas compartment was determined by circulating the gas through a Beckman Acculab-8 Infrared Spectrometer, operated at the 7.2 μm absorption band. The spectrometer was calibrated by means of known SO_2-air mixtures prepared by a specially constructed gas-mixing manifold. Since SO_2 is heavier than air, a precaution was necessary to prevent SO_2 from flowing out of the gas compartment while the gates were open for allowing the drops to fall through. This was achieved by filling the lowest tube section with Freon-12 gas (CCl_2F_2, an inert water insoluble gas of specific gravity 4.2 times larger than that of air). The distance that SO_2 counter-diffuses into the Freon gas during the short period the chamber was kept open to allow passage of the drops has negligible compared to the length of the gas column. It was also assumed that the distance between the lower gate of the gas compartment and the receptacle for the drops, which was about 0.60 m, was short enough (considering the relatively large drop fall velocities) to insure that the amounts of SO_2 scavenged by the drops in the gas compartment desorbed during their fall below the gas compartment was negligibly small.

The drops, which fell through the gas compartment, were collected in a small glass receptacle located at the lower end of the Freon filled portion of the plexiglass tube system. This receptacle contained a very shallow layer of doubly distilled and deionized water of exactly known volume. In contact with this water was the glass electrode (Orion 91–03) of a pH meter (Orion 901) which constantly monitored the change in pH of the water in the receptacle.

Typically, during one run, the pH varied from about 5.5 to a value near 4, the latter depending on the pressure of the SO_2 in the gas compartment, the drop size, the temperature and the residence time of the drops in the SO_2. This time was varied by choosing two gas compartments of different lengths, one of which was 0.420 m and another 1.525 m. From the change in pH of the solution, the total amount of sulfur in the collected solution was computed, and from that the total amount of sulfur and the amount of HSO_3^- in the drops were computed from the relations given in the Appendix. HSO_3^- can be considered the only species present in the solution studied under the condition that $3 \leq pH \leq 5.5$.

The results obtained from the pH measurements were compared with three additional quantitative chemical methods devised for determining the total sulfur in an aqueous solution.

In the first method, the solution containing the scavenged SO_2, was converted by oxidation with hydrogen peroxide (H_2O_2) to a solution of sulfuric acid (H_2SO_4). The resulting solution was titrated with a standard solution of sodium hydroxide (NaOH), using as an indicator a mixture of bromocresol-green and methyl-red. (The NaOH solution was standardized by means of a standard solution of potassium hydrogen-phtalate.)

The second method also involved the conversion of SO_2 into H_2SO_4 by the addition of H_2O_2. The sulfate ion ($SO_4^=$) thus generated was precipitated as barium sulfate ($BaSO_4$) by the addition of a solution of barium chloride ($BaCl_2$) and gelatin, which aids the formation of crystals of the same size uniformly suspended in solution. Using a Beckman DU spectrometer operated at a wavelength of 0.42 μm the depletion of radiation due to the presence of $BaSO_4$ crystals in the path of light passing through the solution was measured. The spectrophotometer was calibrated by means of a set of standard sulfate solutions.

In the third method the amount of sulfur was determined by adding $NaHgCl_4$ to the solution containing the scavenged SO_2. This complexes to the bisulfite ion (HSO_3^-) and prevents the desorption of SO_2 to the air. Subsequently, pararosaniline in a dilute HCl solution was added. The intensity of the purple red color resulting from complexing between HSO_3^- and pararosaniline was then determined by means of a Beckman DU spectrophotometer operated at a wavelength of 0.56 μm. A set of standard solutions served to calibrate the spectrometer.

After completion of each scavenging experiment the plexiglas tube system including the gas compartment was cleaned by circulating the air through a specially constructed set of sodium hydroxide scrubbers. To test the purity of the air, blank tests were conducted by allowing water drops to pass through the cleaned plexiglas system and by testing the water for traces of sulfur.

In the present experiment, the SO_2 concentrations in the gas compartment ranged between 1 and 50%, and the water drops had temperatures which ranged between 13 and 15°C. No appreciable oxidation to $SO_4^=$ took place inside the water drops during their brief exposure to SO_2.

3. Philosophy of present approach

Before summarizing the results obtained by the present experiment, it is necessary to justify the philosophy on which the experimental approach is based. Thus, we realize that under atmospheric conditions trace gas scavenging proceeds at all pressure and temperature levels in the troposphere rather than only at sea level temperature and pressure at which the present experiment was carried out, and it proceeds at SO_2 gas concentrations which are considerably smaller than those which existed in the gas compartment of our present experimental set-up.

We also realize that considerable difficulties are involved in building large low-temperature and low-pressure chambers. Equally great are the difficulties involved in carrying out experiments in which single free falling drops are exposed to trace gases at the low concentrations typical for the atmosphere, as the amount of gas scavenged under such conditions would be very small indeed and therefore extremely difficult to analyze quantitatively unless they fall over long distances difficult to duplicate under laboratory conditions.

For these reasons we approached the gas scavenging problem along two lines: first, we formulated a theoretical framework by which the amount of trace gas scavenged by a water drop of a given size could be computed theoretically for any temperature and pressure level in the atmosphere and for any trace gas concentration. This theoretical model has been presented by Baboolal *et al.* (1981).

Second, we attempted to verify experimentally this theoretical model when evaluated for laboratory conditions at which gas scavenging can be studied quantitatively with relative ease. We made the assumption that the theoretical model, once verified for sea level temperatures and pressures and for the relatively large trace gas concentrations required for the laboratory experiment, would also be applicable to temperatures, pressures and trace gas concentrations lower than those studied experimentally. This was possible since the model depends on pressure and temperature only implicitly through the gas diffusivity of SO_2 and the equilibrium constants K_H, K_1 and K_2 (defined in the Appendix) whose pressure and temperature dependence are well known.

Somewhat more intricate is the problem of applying the theoretical results to lower gas concentrations. It is well known that clustering of molecules takes place at high gas concentrations and at the gas-liquid interface, and that at large solute concentrations solute-solute and solute-solvent interac-

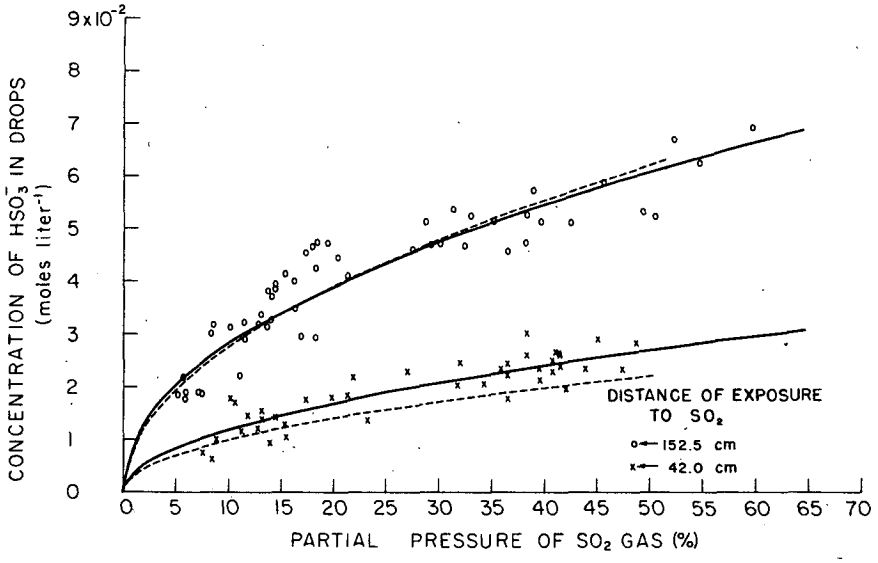

FIG. 1. Variation of the concentration of HSO_3^- in a freely falling drop of 300 ± 20 μm radius as a function of SO_2 concentration in the gas phase; (×) pertain to present experiment for 0.15 ± 0.01 s exposure time; (○) pertain to present experiment for 0.72 ± 0.05 s exposure time. The solid lines are the least-squares fit to experimental data, the dashed lines the theoretical predictions from the theory of Baboolal and Pruppacher (1981).

tions must be expected in the liquid phase. Such interactions are expected to affect the diffusion of gas molecules through the gas phase and across the drop surface into the water. However, it is also well known that significant interactions of this type are confined only to high solute concentrations, and rapidly decrease with decreasing concentration. Since the theory of Baboolal *et al.* (1981) does *not* take into account deviations from the behavior in an ideal gas and an ideal solution, any disagreement between experiment and theory, if it exists at all, would be confined to conditions of high gas concentrations where high solute concentrations are also expected. Thus, if agreement between experiment and theory is found for the high gas concentrations studied in the present experiment, application of the theory to lower gas concentrations may then be justified.

4. Results and discussion

The results of our experimental study are summarized in Fig. 1. One notices from this figure that, despite a fair amount of scatter, the data clearly exhibit a trend represented by an increase in concentration of HSO_3^- in the drop with increasing SO_2 concentration in the gas phase. This trend is found for both the short and the long compartments. We also note that a longer time of exposure to SO_2 results in a significantly larger amount of HSO_3^- in the drop. A least-square fit to the data is also given in Fig. 1. The scatter in the experimental data is due to the combined effects of variations in drop size, reflecting themselves in a variation of the drop fall-speed and exposure time to SO_2, and small variations in the relative humidity in the air, which affect the drop temperature and thus the drop's capability to absorb gas (the latter increasing with decreasing drop temperature).

In Fig. 1, comparison also is made between the least-squares fit to the observed data and the values predicted by the theory of Baboolal *et al.* (1981) evaluated for our experimental conditions. As a basis for this evaluation we used the data derived by Baboolal[3] for a 305.5 μm radius drop and a drop temperature of 20°C. In doing so, we assumed that the flow field inside and outside a drop of 305.5 μm would differ only negligibly from the flow fields for drops of 300 ± 20 μm used in the present experiment. However, a slight temperature correction was needed as the experimental drop temperature was 14 ± 1°C as compared to a drop temperature of 20°C assumed by Baboolal. This adjustment of the curves was done by computing the equilibrium concentration for HSO_3^- in solution for 14°C and by noting that the curves $[HSO_3^-]$ versus time for a given $[SO_2]_g$ are essentially parallel over the time interval considered.

We also note from Fig. 1 that, within the experimental scatter, satisfactory agreement exists between theory and experiment both with respect to the trend as well as with respect to the absolute value of HSO_3^-

[3] Baboolal, L., 1980: private communication.

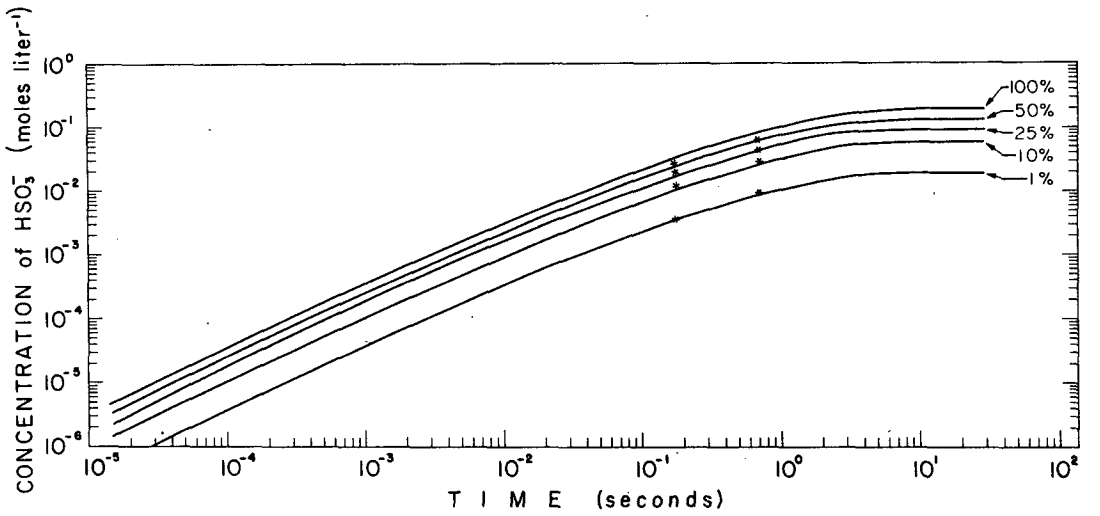

FIG. 2. Variation of the concentration of HSO_3^- in a freely falling drop of 300 ± 20 μm radius as a function of exposure time to SO_2 in the gas phase, for different SO_2 gas concentrations under laboratory conditions. The theoretical predictions by the model of Baboolal and Pruppacher (1981) shown by the solid lines are compared with values from the present experiment given by asterisks.

concentration in the drop. This agreement between experiment and theory also is expressed by means of Fig. 2 where the concentration of HSO_3^- is plotted as a function of time for various SO_2 concentrations in the gas phase. We note from Fig. 2 that with increasing exposure time to SO_2 the concentrations of HSO_3^- inside the drop rapidly approaches the saturation concentration which can be derived from the equilibrium relations in the Appendix.

Although we admit that additional experiments are necessary at other gas concentrations and for drop sizes different from those used in the present experiment, the present experiment does suggest sufficient justification for applying the theoretical model of Baboolal *et al.* (1981) to atmospheric conditions in order to describe the scavenging of SO_2 by cloud and small raindrops. However, as mentioned by Baboolal *et al.*, their model does not apply to drops $\geq$ 500 μm radius since drops larger than this size deviate from spherical shape, and since for large drops, no theoretical flow fields outside and inside the falling drop are available. In order to determine the rate at which gases are scavenged by such large drops, one must rely entirely on experimental measurements. It also must be pointed out that in the present experiments, as well as in the model of Baboolal *et al.* (1981), turbulence in the environment was not considered. From simple consideration, one suspects that turbulence would enhance the rate at which drops scavenge trace gases.

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APPENDIX

Determination of [S], [$SO_2 \cdot H_2O$], [HSO_3^-] and [$SO_3^=$] from Measured Concentrations of [H^+]

For experimental conditions, sulfur was present in the water samples as $SO_2 \cdot H_2O$, HSO_3^- and $SO_3^=$, according to the following equilibrium relations:

$$(SO_2)_g + H_2O \overset{K_H}{\rightleftarrows} SO_2 \cdot H_2O, \qquad K_H = \frac{[SO_2 \cdot H_2O]}{[SO_2]_g}, \tag{A1}$$

$$SO_2 \cdot H_2O \overset{K_1}{\rightleftarrows} H^+ + HSO_3^-, \qquad K_1 = \frac{[H^+][HSO_3^-]}{[SO_2 \cdot H_2O]}, \tag{A2}$$

$$HSO_3^- \overset{K_2}{\rightleftarrows} H^+ + SO_3^=, \quad K_2 = \frac{[H^+][SO_3^=]}{[HSO_3^-]}, \tag{A3}$$

which after some manipulation and use of the condition for electroneutrality $[H^+] = [HSO_3^-] + 2[SO_3^=]$ gives

$$[SO_2 \cdot H_2O] = \frac{[H^+]^3}{2K_1K_2 + K_1[H^+]}, \tag{A4}$$

$$[HSO_3^-] = \frac{[H^+]^2}{2K_2 + [H^+]}, \tag{A5}$$

$$[SO_3^{=}] = \frac{K_2[H^+]}{2K_2 + [H^+]}. \quad \text{(A6)}$$

Since the total amount of sulfur is given by

$$[S] = [SO_2 \cdot H_2O] + [HSO_3^-] + [SO_3^{=}], \quad \text{(A7)}$$

we find from Eq. (A4)–(A6) that

$$[S] = \frac{[H^+]^3 + K_1[H^+]^2 + K_1K_2[H^+]}{K_1(2K_2 + [H^+])}. \quad \text{(A8)}$$

After the drops passed through the gas chamber with SO_2 they were collected in a receptacle which already contained 20.00 cm^3 of water. $[H^+]$ of this solution mixture was then measured. If we designate the concentration of total sulfur in the collecting receptacle and in the drops as $[S]_{coll}$ and $[S]_{drop}$, respectively, and the volume of the drops as V_{drop} in cm^3, mass conservation for sulfur yields

$$[S]_{drop} = [S]_{coll}(V_{drop} + 20)/V_{drop}. \quad \text{(A9)}$$

Since $[H^+]$ is measured in the collector, $[S]_{coll}$ can be determined from Eq. (A8). The drops, N in number and of uniform radius a, have a volume given by

$$V_{drop} = N(4/3)\pi a^3, \quad \text{(A10)}$$

where a is expressed in centimeters.

An expression for $[S]_{drop}$ in terms of quantities measured in the experiment can be given by

$$[S]_{drop} = \left\{\frac{[H^+]^3 + K_1[H^+]^2 + K_1K_2[H^+]}{K_1(2K_2 + [H^+])}\right\} \times \left\{\frac{N(4/3)\pi a^3 + 20}{N(4/3)\pi a^3}\right\}. \quad \text{(A11)}$$

To determine $[HSO_3^-]$ in the drops, the following approximations, which are justifiable at pH values less than 5.5, simplify the derivation:

$$K_2 \ll [H^+], \quad \text{(A12)}$$

$$[H^+] \approx [HSO_3^-]. \quad \text{(A13)}$$

Using the above, Eq. (A8) simplifies to

$$[S]_{drop} = \frac{[HSO_3^-]_{drop}^2 + K_1[HSO_3^-]_{drop}}{K_1}. \quad \text{(A14)}$$

This is quadratic in $[HSO_3^-]_{drop}$ and has the solution

$$[HSO_3^-]_{drop} = \tfrac{1}{2}\{-K_1 + (K_1^2 + 4K_1[S]_{drop})^{1/2}\}. \quad \text{(A15)}$$

Eqs. (A15) and (A11) allow the computation of $[HSO_3^-]$ inside drops that have been exposed to SO_2, in terms of the pH of the drops in the collector.

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