The Absorption of Low Concentrations of Sulphur Dioxide into Aqueous Solutions

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ABSTRACT

The rate of deposition of gas-phase SO_2 to a variety of aqueous solutions has been measured. The deposition rate is unaffected by relative humidity. Some salts may cause a 3-fold decrease in deposition rate as the ionic strength changes from 0.1 M to 0.8 M. Solution pH has the greatest influence causing a change from gas-phase diffusion control to solution phase diffusion control of deposition between pH 4 and pH 2. Indirect evidence has been obtained that suggests that the catalysis of SO_2 oxidation in solution by Mn(II) ions is slow with respect to SO_2 diffusion into solution. The practical implications of these results are discussed.

Introduction

The transfer of sulphur dioxide (SO_2) from the gas phase to the aqueous phase is of importance in several steps of the sulphur cycle. The process of washout of SO_2 by raindrops, which can account for up to 70% of sulphate in the rainwater of polluted areas (Beilke & Georgii, 1967), obviously involves a transfer of SO_2 from the gas phase to the aqueous phase. A similar transfer is necessary prerequisite to SO_2 oxidation in cloud and fog droplets, while oceanic absorption of SO_2 depends upon this transfer. A less obvious step involving aqueous solution of SO_2 is the dry deposition of SO_2 to other surfaces on the land. At most natural humidities, solid surfaces are coated with a thin film of water thus it is likely that the first step in SO_2 deposition to these surfaces is a gas-solution transfer.

In an earlier publication (Spedding, 1972) the velocity of deposition of SO_2 into seawater was measured. The data obtained confirmed the theoretical calculations of Liss (1971) who suggested that SO_2 exchange at almost all environmental air-water interfaces would be controlled by gas phase resistance. The present paper represents an attempt to further extend these studies to aqueous solutions representing a wide range of physical and chemical properties.

Experimental

The concentration of SO_2 found in the polluted atmosphere is generally quite low (less than 100 $\mu g\ m^{-3}$). The best methods for studying the gas at such low concentrations are radiochemical, using $^{35}SO_2$. In the present work all the labelled SO_2 was handled in a nitrogen mixture. SO_2 was obtained in 5 mCi amounts from the Radiochemical Centre, Amersham, England in glass ampoules. The following technique was used to mix SO_2 with nitrogen using the apparatus shown in Fig. 1.

The ampoule was placed at position A on the vacuum line and evacuated with taps 1, 2, 3 and 4 open and taps 5, 6 closed. The ampoule was maintained at liquid nitrogen temperatures which solidified the SO_2 (F.P. 200°K). Tap 3 was closed to close off the space above the ampoule and its seal was broken with a glass enclosed magnet. The liquid nitrogen bath surrounding the ampoule was removed and the SO_2 allowed to come to ambient temperature. The U-tube was cooled in liquid nitrogen and the SO_2 transferred into it by closing Tap 2 and opening Tap 3. A gas cylinder was attached

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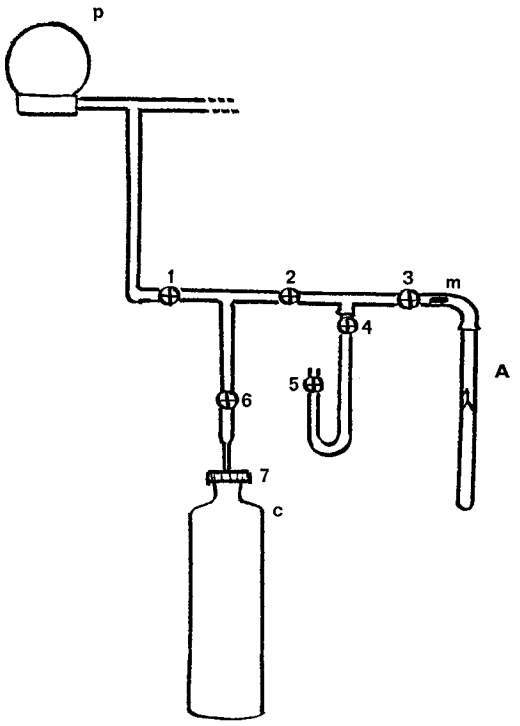

Fig. 1. Apparatus used to transfer $^{35}SO_2$ from break-seal ampoule to gas cylinder. *P*, rotary oil pump; *C*, gas cylinder; *M*, glass-enclosed magnet; *A*, break-seal ampoule of $^{35}SO_2$.

and evacuated through Taps 1, 6 and 7. Taps 1, 3 were closed and Taps 2, 4 opened and the SO_2 allowed to sublime. When all the solid SO_2 had vapourised, nitrogen was allowed to enter through Tap 5 and bring the cylinder to atmospheric pressure. Tap 7 was closed and the cylinder pressurised with oxygen-free nitrogen to about 50 atmospheres.

The method used to determine absorption rate was similar to that described by Spedding (1972). 50 ml volumes of aqueous solution were exposed to a $^{35}SO_2$/air mixture which was maintained at a constant flow through the apparatus. Humidity was adjusted by splitting the air flow through two gas wash bottles one of which was filled with water and the other with silica gel. By varying the flow through each the humidity of the total gas flow could be controlled. $^{35}SO_2$/nitrogen mixture was bled in and 30% of the mixture sampled by passage through a gas-wash bottle containing 1 vol. hydrogen peroxide. At the completion of any experiment a volume of this solution was counted in a liquid scintillation spectrometer to determine the SO_2 dosage (the product of SO_2 concentration and time). The remainder of the mixture passed into a 100 ml 3-necked flask which contained the test solution (27 cm^2 surface area). A pH electrode protruded through one neck which also gave access to two 1 mm bore plastic tubes. The solution was pumped through these with a peristaltic pump into a glass scintillation flow cell (NE805, Nuclear Enterprises Ltd., Great Britain) and the ^{35}S activity was monitored by a single channel beta-spectrometer. The ^{35}S activity and pH were recorded on a multichannel chart recorder. The apparatus may be seen in the paper of Spedding (1972).

The results of the experiments were expressed as deposition velocities (V_g). Such a parameter is ideally suited to environmental surfaces where the flux does not depend on the amount of material already deposited (Chamberlain, 1960). As only small amounts of SO_2 were absorbed into solution the value of V_g remained constant throughout each experiment. V_g is related to the flux by the equation:

$$V_g = \frac{\text{rate of deposition per unit area}}{\text{dosage}}$$

$$= J/C \qquad J = \text{flux of } SO_2 \text{ per unit area}$$

$$C = \text{gas concentration of } SO_2$$

Experiments were of 1 000 s duration and the non laminar gas flow was kept at constant 65 ml s^{-1}. Temperature was maintained at $20° \pm 2°C$. In the initial work it was possible to establish that a linear relationship existed between gas concentration and absorption rate over the concentration range used in the experiments (600–300 $\mu g\ m^{-3}$). The rate of desorption from solution was determined by adding a known amount of sodium sulphite and a $^{35}SO_2$ "spike". Samples were removed from the solution at regular intervals and the amount of sulphur present determined by liquid scintillation counting. The effect of oxidation of S(IV) to S(VI) was eliminated by using high concentrations of S(IV) and only the initial rates of dissolution. The apparatus was similar to that described for the uptake experiments except that no $^{35}SO_2$ was introduced into the gas flow.

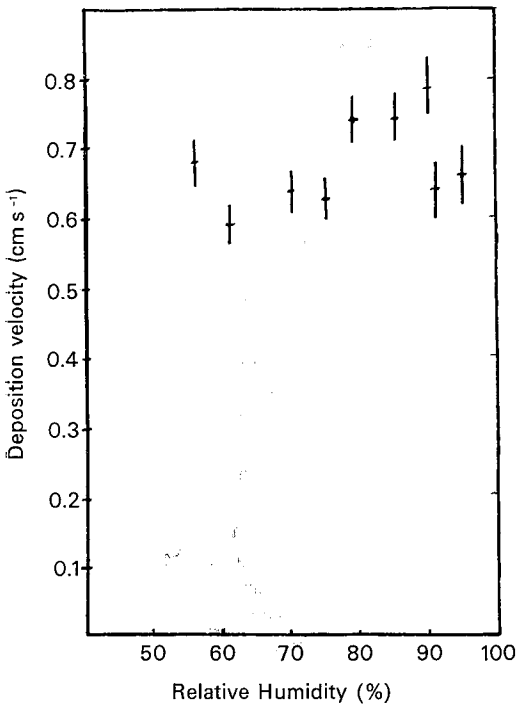

Fig. 2. Rate of deposition of SO_2 into de-ionised water as a function of relative humidity at $20 \pm 2°C$.

Results and discussion

The split air flow described in the previous section enabled the relative humidity to be varied between 50% and almost 100%. As can be seen in Fig. 2 there does not seem to be any significant variation with relative humidity in the rate of deposition of SO_2 into aqueous solution. This differs from the significant increase in deposition velocity that is found in the deposition of SO_2 on to metals (Spedding, 1969). If such an effect had been found in the results for uptake by aqueous solution, it would have given reasonable support for the prior formation of an SO_2-water aerosol, a possibility suggested by Liss (1972).

No effect of ionic strength on the deposition velocity was seen at pH values where gas phase diffusion control dominated (Table 1). At pH values where solution phase reactions were important some solutions ($NaNO_3$, $(NH_4)_2SO_4$, $MnSO_4$) caused a decrease in V_g with increase in ionic strength from 0.01 M to 0.8 M, the change in V_g being no more than a factor of three.

Table 1. *The rate of deposition of SO_2 into $NaClO_4$ solution at pH 5.5*

$NaClO_4$ concentration (M)	Deposition velocity (cm s^{-1})
1.0	0.65
0.1	0.64
0.01	0.66

It has been shown previously (Liss, 1971; Brimblecombe & Spedding, 1972) that at pH values above pH 4, the dissolution of SO_2 is largely controlled by diffusion in the gas phase. However, at pH values lower than this the dissolution becomes controlled by diffusion through the liquid boundary layer. The decrease in V_g as the rapid gas diffusion-controlled dissolution is replaced by the slower liquid diffusion-controlled process is seen in Fig. 3. Thus it is at low pH values that solutes can be seen to exert an effect on the rate at which SO_2 dissolved. Through addition of oxidizing agents to the solution the effective diffusion rate of sulphur species can be increased so that the absorption rate approaches the gas phase diffusion limit even at low pH values. With 1 vol H_2O_2 solution at pH 2.3 the value of V_g was 0.59 cm s^{-1}

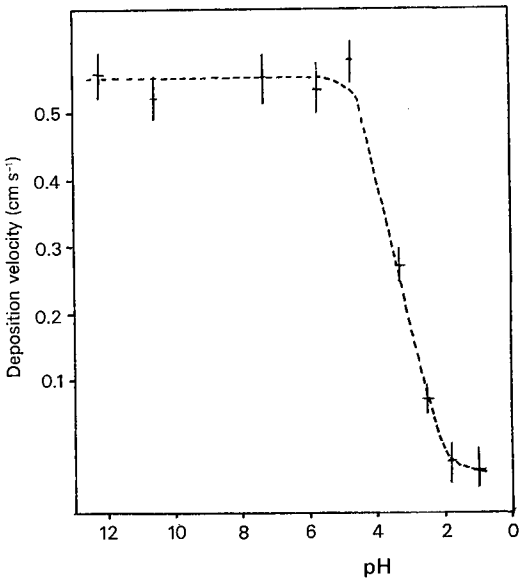

Fig. 3. Rate of deposition of SO_2 into perchlorate solutions as a function of pH.

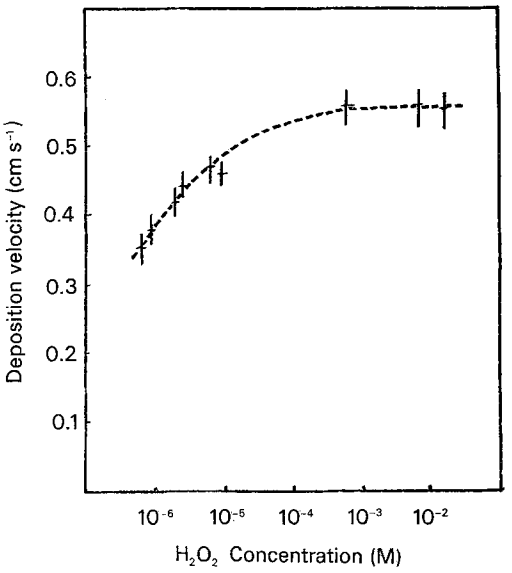

Fig. 4. Rate of deposition of SO_2 into H_2O_2 solutions at pH 3.3 as a function of H_2O_2 concentration.

while that for distilled water was 0.11 cm s^{-1}. At the lower values of pH 1.6, V_g for 1 vol H_2O_2 was 0.50 cm s^{-1} which may be compared with 0.07 cm s^{-1} for distilled water at this pH.

The effect of H_2O_2 concentration on the deposition velocity at a constant pH was examined over a wide range of H_2O_2 concentrations. Its action was significant even at extremely low concentrations.

A decrease in its influence on V_g could only be found where it was depleted before the 1 000 s experiments were over. These results are displayed in Fig. 4. Addition of small amounts of I_2/KI solution displayed similar behaviour. However the addition of manganese sulphate did not increase the absorption rate of SO_2 to its gas phase diffusion limit. This would be expected if the manganese(II) ion could induce an autoxidation of SO_2 which was fast with respect to diffusion across the liquid boundary film. It is evident from this that manganese-catalysed oxidation of SO_2 is slow on a diffusion time scale and this agrees well with the kinetic studies of Penkett (1972). The results of all the experiments described represent initial deposition velocities. They can be compared with overall values derived from the work of Terraglio & Manganelli (1967) where V_g at a SO_2 concentration of 810 μg m^{-3} is about 0.56 cm s^{-1}, a favourable agreement with the values obtained in the present work.

Table 2. *Half-lives for the loss of SO_2 from solution*

Solution pH	Half life (s)
2.0	600 (10 min)
2.5	1 020 (17 min)
3.0	2 200 (37 min)

The rate of desorption was examined under conditions similar to those used for the absorption experiments. Concentrations in solution were kept high (about 10^{-3} M, S(IV) and above) to minimise problems arising from oxidation of the S(IV) species. Table 2 gives the half lives for desorption at a number of pH values. Spedding (1972) could find no desorption of SO_2 dissolved in seawater when air was passed over the solutions. His findings are not contradicted by the present work from which it would be predicted that desorption would be slow from alkaline solution. The observed decrease in rate of loss of SO_2 with increasing pH from solution would also be expected from the fact that the concentration of the aquated SO_2 molecule decreases with acidity. At high concentrations ($10^{-2} - 10^{-4}$ M) the rate of desorption was linearly related to $H_2O \cdot SO_2$ concentration in solution.

Conclusions

Over the land vegetation would appear to provide the greatest surface area for SO_2 absorption, while in the marine environment the sea surface must represent the most likely area for absorption. Recently, Garland et al. (1973) have determined the deposition velocity of SO_2 from the air above a grass-covered field using the SO_2 concentration gradient in that air mass. They obtained a value for the deposition velocity of 0.85 cm s^{-1}. This value is similar to that obtained for SO_2 deposition to seawater in moderately-turbulent conditions. It would thus seem that both the land and the sea have similar abilities to absorb SO_2.

Within the atmosphere it is to be expected that the aqueous phase will vary from near-saturated salt solutions formed from hygroscopic salt nuclei, to almost pure water in equilibrium

with the atmospheric gases. The pH of the resultant aqueous droplets will exert the greatest effect on SO_2 absorption, especially for particles of pH lower than pH 4. The solution, and subsequent oxidation of SO_2 in droplets results in a decrease in pH hence the buffer capacity of the salts in atmospheric droplets becomes of considerable importance.

Although it has been shown that relative humidity has no measurable effect on SO_2 deposition into aqueous solution, it could have an indirect effect at pH values where deposition is controlled by solution phase reactions. The concentration of a salt solution in a droplet formed from a hygroscopic salt is dependent upon the relative humidity of the air about that droplet. For relative humidities close to the humidity at which a hygroscopic salt particle becomes a saturated solution it would be expected that SO_2 deposition would be lower than at higher humidities, where the ionic strength of the droplet would be lower.

The observation that a $MnSO_4$ solution could not increase the deposition velocity for SO_2 at low pH values as could H_2O_2 and I_2 is of particular importance in the atmospheric chemistry of SO_2. It implies that the rate-limiting step in the aqueous oxidation of SO_2 in the presence of a very potent oxidation catalyst (Foster, 1969) is a solution reaction. The rate of exchange of SO_2 from the gas phase to such droplets is thus of only minor importance, and the need to obtain accurate rate data on S(IV) oxidation in the presence of Mn(II) in a variety of salt solutions becomes of considerable importance.

Acknowledgements

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ПОГЛОЩЕНИЕ НИЗКИХ КОНЦЕНТРАЦИЙ ДВУОКИСИ СЕРЫ ВОДЯНЫМИ РАСТВОРАМИ

Измеряется скорость поглощения SO_2 в зависимости от типа водяного раствора. Скорость поглощения не зависит от относительной влажности. Некоторые солевые растворы приводят к 3-кратному уменьшению скорости поглощения по мере того, как ионная концентрация изменяется от 0,1 М до 0,8 М. Величина pH раствора оказывает наибольшее влияние, вызывая изменение диффузии от газовой фазы до растворной фазы при изменении от pH4 до pH2. Получено косвенное доказательство того, что катализ окисления SO_2 в растворе с помощью ионов Mn (11) является медленным по сравнению с диффузией SO_2 в раствор. Обсуждаются практические следствия этих результатов.