

OXIDATION OF SO₂ IN AQUEOUS DROPLETS: MASS-TRANSPORT LIMITATION IN LABORATORY STUDIES AND THE AMBIENT ATMOSPHERE*

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Abstract—Despite numerous laboratory investigations, the aqueous phase oxidation of SO₂ remains ill-understood. A major reason for this is the failure to treat properly the combined problem of mass transport and chemical reaction. This problem has not been adequately addressed either by experiments with bulk solutions or by experiments with aqueous droplets that have been undertaken in order to circumvent the mass-transport problem associated with bulk solutions. The conclusions of these laboratory investigations conflict with each other and report reaction rates which are considerably different from those that would pertain to the same reactions in the ambient atmosphere.

In this paper we apply the theoretical analysis that has been developed to describe mass transport and reaction of SO₂ in aqueous droplets (Schwartz and Freiberg, 1981) to an analysis of the data of two laboratory studies of this reaction system. It is shown that mass-transport limitation (both gas-phase and aqueous-phase) in the experiment of Barrie and Georgii (1976) may have reduced the measured rates by 20% to as much as an order of magnitude from the intrinsic rate. In the experiment of van den Heuvel and Mason (1963) gas-phase mass-transport limitation is shown to have prevented the steady-state reagent concentration from having been achieved in the contact times employed. Consequently, the rate constants derived from these data by Scott and Hobbs (1967) are too low.

Application of the analysis of Schwartz and Freiberg (1981) to an examination of SO₂ oxidation in clouds and fogs indicates that the mass-transport limitation of the oxidation rate is not significant except under conditions of very high oxidation rates, e.g. at high ozone or H₂O₂ concentration.

1. INTRODUCTION

Both by mass and by number, sulfate particles constitute a significant fraction of anthropogenic atmospheric aerosol (Junge and Scheich, 1969; Charlson *et al.*, 1978; Cunningham and Johnson, 1976). It is generally agreed that most of this particulate sulfate is not emitted directly into the atmosphere but results from the oxidation of gaseous precursors, principally SO₂ (Altshuller, 1976; Winchester, 1980; ISSA, 1978). The conversion of SO₂ to sulfate may occur either by homogeneous gas-phase reaction or by heterogeneous reaction, i.e. reaction in solution phase in aqueous aerosols or cloud droplets or on the surface of solid aerosols. Although there is now considerable evidence from both laboratory investigations and field studies implying that heterogeneous reactions of SO₂ are important in the atmospheric formation of aerosol sulfate (ISSA, 1978), the quantitative understanding of the rates of these processes remains rather primitive. By contrast, the quantitative understanding of the

rates of homogeneous gas-phase reactions of SO₂ is rather well developed (Calvert *et al.*, 1978). This is due in large part to the fact that unlike the homogeneous formation of sulfate, the heterogeneous formation of sulfate may occur by any of a large number of separate and distinct paths, e.g. uncatalyzed oxidation, oxidation catalyzed by transition metal ions, reaction with oxidants such as O₃ or H₂O₂, and surface catalyzed reaction. But there is also another complicating factor present in the case of these heterogeneous aqueous processes, viz., the finite rate of mass transport processes within each phase and across phase boundaries. This factor pertains both to the interpretation of relevant laboratory studies and to the rates of these processes in the ambient atmosphere.

This paper addresses the influence of mass-transport limitation on the rate of oxidation of SO₂ to sulfate in aqueous solutions. In an accompanying paper [Schwartz and Freiberg (1981) (SF)] we have presented a theoretical framework that permits evaluation of the magnitude of this limitation for reaction in aqueous droplets. Here we review the pertinent literature from this perspective and point out that inadequate consideration of mass-transport effects is responsible in large measure for differences in interpretation of laboratory experiments, thus contributing to

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the primitive state of the present day quantitative understanding of heterogeneous aqueous reactions. Then, using the framework developed in SF, we analyze experiments reported in the literature and point out the relative importance of mass transport and oxidation reaction in the determination of the overall rate of conversion in these experiments. Finally, we examine mass-transport limitation to the rate of oxidation of SO₂ in clouds and fogs.

2. LITERATURE REVIEW

Over the years numerous experimental studies have been conducted to determine the rate of oxidation of SO₂ in aqueous solution. These studies may be divided into two classes, those employing bulk solutions and those utilizing small droplets. In studies with bulk solutions there is generally an excess of dissolved sulfur-IV, and mechanical mixing is employed to supply O₂ to the aqueous solution to replenish this reagent as it is consumed. In the case of fast reactions an adequate rate of mixing may not be achieved. Studies are performed with droplets to enhance the rate of mass transport and to more closely simulate reactions in atmospheric aerosols by employing both SO₂ and O₂ as gaseous reagents. However, despite the numerous investigations, there remains considerable disagreement over the role of the various steps in the oxidation process in determining the rate of reaction measured in laboratory studies. We review here the important experimental studies of SO₂ aqueous oxidation, with emphasis upon the role of mass-transport effects.

Experiments with bulk solutions

Many investigators have attempted to determine the rate constant for oxidation of SO₂ by performing experiments with bulk solutions (Reinders and Vles, 1925; Fuller and Crist, 1941; Basset and Henry, 1935; Anderson and Johnstone, 1955; Junge and Ryan, 1958; Neytzell de Wilde and Taverner, 1958; Schroeter, 1963; Bracewell and Gall, 1967; Beilke *et al.*, 1975; Brimblecombe and Spedding, 1975; Chang *et al.*, 1978; Barona *et al.*, 1978; Larson *et al.*, 1978; Penkett *et al.*, 1979). Such experiments were early shown to be vulnerable to mass-transport effects in one or both phases. For example, Reinders and Vles (1925) showed how the values of factors which impact the rate of reaction (e.g. the rates of diffusion mixing of O₂ and SO₂, and the rate of evolution of SO₂ into the atmosphere) were affected by variations in stirring velocity and in the surface area of the bulk. Much later, Schroeter (1963), studying the effect of air flow rates on the oxidation rate of SO₂, concluded that an increase in flow rate increased the oxidation rate asymptotically up to a certain limiting value, which he took to represent the intrinsic oxidation rate. The role of mass transport in the experiments of Anderson and Johnstone (1955) and of Junge and Ryan (1958) has

been noted also by Cheng *et al.* (1971), and by Barrie and Georgii (1976).

Oxidation of sodium sulfite was examined recently by Barona *et al.* (1978), who found that the oxidation rate was dependent upon the hydrodynamics of the gas-liquid interface in an agitated solution. Under these conditions the rate of oxidation was controlled by the rate of introduction of O₂ into the aqueous phase. On the other hand Larson *et al.* (1978) interpreted the rate of sulfur-IV oxidation in a similar experiment, in which O₂ was bubbled through sulfite solution, as being controlled entirely by the rate of the oxidation step. In yet another recent study (Penkett *et al.*, 1979), the air oxidation of SO₂ (1×10^{-3} M) was studied with no effort to replenish O₂ ($[O_2]_{\text{sat'd}} = 3 \times 10^{-4}$ M).

Because of the difficulties in ascertaining the intrinsic rate of oxidation from studies in bulk solutions, faulty conclusions may be reached when the results of experiments performed in bulk are projected onto phenomena occurring in droplets. For example, Chang *et al.* (1978) observed a rate of carbon-catalyzed sulfate formation in a bulk sulfurous acid solution that was independent of pH. This finding has prompted the suggestion that this mechanism was a means for "the production of acid in the presence of acid" in atmospheric droplets that could account for the production of sulfate in aqueous droplets in low [NH₃] environments. However, such speculation has been shown to be incorrect (Freiberg, 1978).

Experiments with droplets

Since the characteristic time of diffusion decreases strongly with the dimension of the system, one approach taken toward measuring the intrinsic oxidation rate of SO₂ has been to work with liquid droplets (van den Heuvel and Mason, 1963; Matteson *et al.*, 1969; Cheng *et al.*, 1971; Johnstone and Coughanowr, 1958; Miller and de Pena, 1972; Barrie and Georgii, 1976; Kaplan *et al.*, 1977; Cains and Carabine, 1978). In such studies one exposes droplets to an atmosphere containing SO₂ and O₂. Because of the limited solubility of sulfur-IV, at least in acidic solutions of atmospheric concern (pH \lesssim 5.6), the rate of oxidation is approximately equal to the rate of uptake of sulfur into the droplet $d[S]/dt$. Experimentally it is generally the rate of uptake that is measured directly.

A principal objective of this approach has been to minimize or eliminate entirely the effect of diffusion on experimental measurements and thereby to simulate reactions in atmospheric aerosols. However, it is far from agreed in the literature that this goal has been achieved. For example, Cheng *et al.* (1971), working with micrometer and sub-micrometer aqueous droplets deposited on Teflon beads, found that the conversion rate was enhanced 12-fold by the use of MnSO₄ as a catalyst instead of NaCl, and concluded from this that the rate of oxidation was controlled entirely by chemical kinetics. However, Huang (1972) argued that

the rate determined in this study was significantly influenced by liquid-phase diffusion.

Van den Heuvel and Mason (1963), working with 0.1–1 mm droplets in an environment containing SO₂ and NH₃, observed a rate of formation of sulfate two orders of magnitude larger than the rate in the absence of NH₃ and concluded that in the aqueous phase SO₂ oxidation is the limiting process. Scott and Hobbs (1967) concurred with this assessment and utilized these data to calculate a rate constant for the “uncatalyzed” oxidation of SO₂. However, Carabine (1972), utilizing the same experimental results, observed that the increase in sulfate mass in the droplet was proportional to the droplet surface area and the exposure time, and concluded that the diffusion in the aqueous phase was the overall controlling factor. Eggleton and Atkins (1972) re-analysed van den Heuvel and Mason’s data, finding that the amount of conversion was proportional to the volume of the droplet, and concluded that the chemical reaction was the limiting process. More recently, Hidy *et al.* (1977) have suggested that the conversion was aqueous-phase diffusion limited, a conclusion which in their opinion “concurrs” with those of previous investigators of the aqueous-phase phenomena.

In contrast to the above investigators, Johnstone and Coughanowr (1958) explicitly addressed the competition of aqueous-phase diffusion and reaction in designing and interpreting their experiment. Working with droplets 0.7 mm in diameter suspended in an SO₂–air mixture, they found the oxidation rate to be aqueous-diffusion controlled under those conditions. But their interpretation was subsequently questioned by Cheng *et al.* (1971).

Evidence that has been adduced that the rate of SO₂ uptake and conversion is controlled by the rate of oxidation includes the dependence of this rate on pH and on the concentrations of SO₂, NH₃, and catalysts (Cheng *et al.* 1971; van den Heuvel and Mason, 1963; Barrie and Georgii, 1976; and Miller and dePena, 1972). However, such a dependence does not necessarily prove that the rate of uptake is entirely chemically controlled. Huang (1972) has suggested that such a dependence may nonetheless be consistent with a mechanism which is diffusion controlled, the concentration dependence arising from a dependence of diffusion rate upon concentration. More fundamentally, the rate of a given reaction system may exhibit a dependence upon chemical parameters and yet be severely aqueous-phase diffusion-limited for reasons entirely consistent with the theoretical understanding of these processes (see Fig. 6 of SF).

A further avenue toward distinguishing between reaction systems that are chemically controlled and those which are diffusion limited is through the dependence of the rate on the droplet size. A rate of uptake in a given droplet proportional to droplet volume, i.e. to the third power of the radius, would argue for a rate that is chemically controlled (Eggleton and Atkins, 1972), whereas a dependence upon a lower

power of droplet radius would imply diffusion limitation (Carabine, 1972; Johnstone and Coughanowr, 1958). However, testing the dependence of the rate upon droplet size requires measurements of quite high precision and/or experimentation over a wide range of droplet radius, conditions that have not been fulfilled in the experiments noted. In this regard we would point out that the difficulty of such studies would be enhanced by other potential size-dependent effects such as solvent evaporation and resultant systematic variation of temperature with droplet size.

In summary, despite an extensive literature, there is a continuing controversy over whether the rate of SO₂ uptake into aqueous droplets is controlled by chemical reaction or by diffusion in the droplet. It is this continuing controversy that led SF to develop readily applicable criteria for ascertaining the presence or absence of diffusion limitation and for determining the magnitude of such limitation. In the following section we apply the treatment of SF to an examination of the laboratory studies of Barrie and Georgii (1976) and van den Heuvel and Mason (1963).

3. APPLICATION TO EXPERIMENTAL DATA

In this section we examine previously reported experimental studies in order to ascertain whether there was significant diffusion limitation in these studies, and, if so, to estimate the extent. Since the analysis that was developed by SF for aqueous-phase diffusion limitation was based on a model of first-order chemical kinetics, application of that treatment will be exact only if the reaction mechanism is first order in sulfur-IV. The rate of the transition-metal catalyzed SO₂ oxidation is thought to be first order in [S(IV)] and in catalyst concentration and inversely proportional to [H⁺] (Hegg and Hobbs, 1978) and thus would fulfill the first-order requirement in a system that was sufficiently well buffered for the pH to be constant. Additionally, while the framework that has been developed will not be exact for oxidation mechanisms that are not first-order in [S(IV)], we may still expect this model to give valuable qualitative insight in the case of other mechanisms as an index of when a more exact treatment is required. Furthermore, for mechanisms that are higher than first order in [S(IV)], the effect of fall-off in reagent concentration as a function of distance into the aqueous medium will be greater than for a first-order mechanism, and hence the estimated error in the rate due to aqueous-phase diffusion limitation will be a lower bound to the actual error. Finally, since gas-phase diffusion limitation depends only upon the flux of the gaseous reagent into the droplet and is independent of the mechanism of chemical reaction in the aqueous phase, the treatment of SF is applicable to any such mechanism. Thus much can be learned by applying the treatment of SF even to quite complicated chemical systems.

Analysis of Barrie and Georgii (1976)

In the recent study of Barrie and Georgii (1976), which has been described in greater detail by Barrie (1975), suspended aqueous droplets of radius 0.105 cm containing specified catalyst concentrations were exposed to air containing 100–1000 ppb SO₂; gas-phase mixing was enhanced by use of fans. After various contact times, exposure was halted and the droplets were analyzed for sulfur content. Typically, the rate of sulfur uptake was initially fairly high and then decreased to a value that remained rather constant over tens of minutes to several hours. Since the solutions were unbuffered, the solution pH decreased during the run; the measured pH agreed closely with that expected for a ratio of [H⁺] to [S] equal to 2. In some runs the initial pH was adjusted with HCl.

The data given by Barrie and Georgii (1976) are sufficiently detailed to permit the analysis of SF to be applied. We have done this for several of their experimental runs, as shown in Table 1. For this analysis we have taken $D_g = 0.126 \text{ cm}^2 \text{ s}^{-1}$ (Andrew, 1955) and $D_a = 1.8 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ (Himmelblau, 1964), which are appropriate to the measurements at 25°C.

First we consider the time required to reach steady state. The characteristic time for establishing the pseudo-steady-state concentration profile in the gas phase, as controlled by gas-phase diffusion is

$$\tau_{d.g.} = a^2/\pi^2 D_g,$$

where a is the droplet radius. Similarly for the aqueous phase the time constant for establishing the steady-state concentration profile is bounded by the characteristic time of aqueous diffusion

$$\tau_{d.a.} = a^2/\pi^2 D_a.$$

For the drop radius 0.105 cm employed by Barrie and Georgii (1976), $\tau_{d.g.}$ and $\tau_{d.a.}$ are 8.9×10^{-3} and 62 s, respectively. The characteristic time associated with gas-phase diffusion of the equilibrium reagent concentration to the droplet is given by

$$\tau_{\text{reag}} = \frac{\pi^2}{3} \eta HRT \tau_{d.g.},$$

where H is the Henry's law coefficient of SO₂ (M atm^{-1}), R is the universal gas constant ($\text{atm M}^{-1} \text{K}^{-1}$), T is the absolute temperature (K), and η is the ratio of the concentration of dissolved S(IV) to that of dissolved SO₂,

$$\eta = 1 + K_{a1}/[\text{H}^+] + K_{a1}K_{a2}/[\text{H}^+]^2.$$

K_{a1} and K_{a2} are the first and second acid dissociation constants of sulfurous acid. Because of the pH dependence of η (Fig. 2 of SF) there is a corresponding pH dependence of τ_{reag} . Values of τ_{reag} calculated for conditions of the several runs presented by Barrie and Georgii at 25°C are given in Table 1 and range from 12 to 145 s.

Based upon the values of $\tau_{d.a.}$ and τ_{reag} , we conclude that under the experimental conditions of Barrie and

Georgii (1976) the steady state condition may be expected to be achieved within a contact time of 1–5 min. This conclusion is borne out by examination of Fig. 1 of Barrie and Georgii (1976), in which the initially high rate of uptake decreases at such times to a lower, nearly constant value. This agreement lends strong support to the application of this treatment to Barrie and Georgii's (1976) experimental conditions.

We now examine possible non-uniformity in the profile of reagent concentration in the gas phase. This is addressed by comparing $\tau_{d.g.}$ with $\tau_{c.g.}$, the characteristic time of chemical reaction referred to the gas phase concentration, with the criterion for gas-phase uniformity being that $\tau_{d.g.} \ll \tau_{c.g.}$; $\tau_{c.g.}$ is evaluated as

$$\tau_{c.g.} = G_\infty/\bar{R},$$

where G_∞ is the bulk gas-phase concentration (M), and \bar{R} is the measured rate of reaction averaged over the volume of the droplet (M s^{-1}).

Values of \bar{R} , taken from the indicated graphs of Barrie and Georgii (1976), and of the corresponding values of $\tau_{c.g.}$ are given in Table 1. It is seen that the condition $\tau_{d.g.} \ll \tau_{c.g.}$ is not fulfilled for all these experiments. The ratio $\tau_{d.g.}/\tau_{c.g.}$ ranges from 6% to as much as 43%, which raises the possibility of significant gas-phase diffusion limitation. To examine this further we have evaluated the ratio of the bulk gas concentration to that at the surface of the droplet, $G(a)$ (Equation 31 of SF)

$$\frac{G_\infty}{G(a)} = \left(1 - \frac{\bar{R}a^2}{3D_g G_\infty} \right)^{-1},$$

under the assumption that gas-phase mass transport is due entirely to molecular diffusion. The resulting values of $G_\infty/G(a)$, which are given in Table 1 and range from 1.2 to 4.2, would imply significant gas-phase diffusion limitation in the absence of stirring. This computation gives theoretical substantiation to the empirical observation (Barrie, 1975) of a four-fold enhancement of the initial rate of uptake of SO₂ with the fans on rather than off. It is beyond the scope of this paper to determine whether the applied gas-phase stirring was sufficient to eliminate completely any gas-phase diffusion limitation to the rate of uptake, and indeed the information presented in the original papers does not permit such a determination. However, since the measured rate was comparable to the diffusion-controlled maximum, especially at the higher rates of uptake, the possibility of such limitation cannot be confidently excluded without experimental confirmation.

We now examine possible diffusion limitation in the aqueous phase. Here we wish to compare $\tau_{d.a.}$ with the characteristic time of chemical reaction referred to the aqueous-phase concentrations, $\tau_{c.a.}$. The criterion for absence of aqueous-phase diffusion limitation is that $\tau_{d.a.} \ll \tau_{c.a.}$. The apparent value of $\tau_{c.a.}$, which approaches the actual value in the absence of aqueous-phase diffusion limitation, may be evaluated as

$$\tau'_{c.a.} = [\text{S(IV)}]_* / \bar{R},$$

Table 1. Examination of gas- and aqueous-phase diffusion limitation in the experiments of Barrie and Georgii (1976)*

Experiment	Catalyst	pH	P _{SO₂} (atm)	τ_{reag} (s)	\bar{R} (M s ⁻¹)	$\tau_{\text{c.g.}}$ (s)	$G_{\infty}/G(a)$	[S(IV)]* (M)	$\tau'_{\text{c.a.}}$ (s)	k' (s ⁻¹)	$q's$	k/k'	k (s ⁻¹)
Fig. 1-C 10 min	MnCl ₂ 10 ⁻⁵ M	3.3	9.0(-7)†	145	2.4(-7)	1.5(-1)	1.2	4.4(-5)	180	5.5(-3)	1.8	1.2	6.6(-3)
Fig. 1-B 10 min	MnCl ₂ 10 ⁻⁴ M	3.1	4.5(-7)	92	1.6(-7)	1.2(-1)	1.3	1.4(-5)	85	1.2(-2)	2.7	1.6	1.9(-2)
Fig. 1-A 10 min	MnCl ₂ 10 ⁻⁴ M	3.0	9.0(-7)	66	4.1(-7)	9.0(-2)	1.5	2.0(-5)	50	2.0(-2)	3.5	2.1	4.1(-2)
Fig. 2-C	FeCl ₂ 10 ⁻⁴ M	2.9	7.0(-7)	59	3.2(-7)	9.0(-2)	1.5	1.4(-5)	43	2.3(-2)	3.8	2.3	5.3(-2)
Fig. 2-B	MnCl ₂ 10 ⁻⁴ M	2.9	7.0(-7)	59	3.8(-7)	7.5(-2)	1.6	1.4(-5)	36	2.8(-2)	4.1	2.6	7.3(-2)
Fig. 2-A	MnCl ₂ , FeCl ₂ 10 ⁻⁴ M, 10 ⁻⁴ M	2.1	7.0(-7)	12	2.5(-7)	1.2(-1)	1.3	2.8(-6)	11	9.0(-2)	7.4	6.8	6.1(-1)
Fig. 2-A	MnCl ₂ , FeCl ₂ 10 ⁻⁴ M, 10 ⁻⁴ M	2.5	7.0(-7)	24	7.5(-7)	3.8(-2)	4.2	5.6(-6)	7.5	1.3(-1)	9.0	9.7	1.3

* The droplet radius was 0.105 cm, corresponding to $\tau_{\text{d.a.}} = 62$ s and $\tau_{\text{d.g.}} = 8.9 \times 10^{-3}$ s.† The notation 9.0(-7) represents 9.0×10^{-7} .

where [S(IV)]* denotes the sulfur-IV concentration at the surface of the droplet. We have evaluated [S(IV)]* as $\eta H p_{\text{SO}_2}$, i.e. taking the gas-phase SO₂ concentration at the surface of the drop to be equal to the bulk concentration, neglecting any possible gas-phase diffusion limitation. Any reduction in the gas-phase concentration would lead to a proportionate decrease in [S(IV)]* and $\tau'_{\text{c.a.}}$. For the determination of η we either have utilized the specified pH or have computed [H⁺] as twice the dissolved sulfur concentration. Values of [S(IV)]* and $\tau'_{\text{c.a.}}$ are given in Table 1; $\tau'_{\text{c.a.}}$ is seen to range from 180 s to as low as 7.5 s. Comparing these values of $\tau'_{\text{c.a.}}$ with values of the characteristic times for hydration, ionization, and achieving Henry's law (Fig. 2 of SF) we find, as anticipated, that chemical reaction is by far the slowest of the several intrinsic steps. On the other hand, comparison of $\tau'_{\text{c.a.}}$ with the characteristic aqueous-phase diffusion time, $\tau_{\text{d.a.}} = 62$ s, shows that the condition for a uniform aqueous-phase concentration profile ($\tau_{\text{d.a.}} \ll \tau'_{\text{c.a.}}$) is not satisfied in any of the experiments presented, and indeed $\tau_{\text{d.a.}}$ exceeds $\tau'_{\text{c.a.}}$ in most of these experiments.

Again the failure to satisfy the criterion for a uniform concentration profile invites more detailed treatment. To this end we have evaluated the effective diffusio-reactive parameter (Equation 20 of SF)

$$q' = a(k'/D_a)^{1/2},$$

where k' was evaluated as $\tau'_{\text{c.a.}}^{-1}$; i.e. the reaction was treated as a first-order reaction in S(IV). [It should be noted that the definition of the first-order rate constant k employed here differs from that employed by Barrie and Georgii (1976), which was based upon a ratio to the SO₃²⁻ ion concentration only. As pointed out by SF, because of the rapid equilibria among the sulfur-IV species in solution it is the rate constant for oxidation based upon the entire pool of dissolved S(IV) that must be considered to be in competition with mass-transport processes.] Values of q' are seen to range from 1.8 to 9.0. Knowing q' and using Fig. 7 or Equation (21a) of SF, we can evaluate k/k' , the ratio of the actual value to the apparent values of the first order rate constant. The values of k/k' given in Table 1 establish that for all the experimental conditions presented by Barrie and Georgii there was significant aqueous-phase diffusion limitation to the rate of uptake. The magnitude of the systematic error in k due to this diffusion limitation ranges from some 20% (for 10⁻⁵ M Mn²⁺ catalyst concentration) to an order of magnitude (10⁻⁴ M each Mn²⁺ and Fe²⁺). It should be re-emphasized that these conclusions hold only if the dominant aqueous phase mixing mechanism was that of diffusion. Barrie (1975) (cf. also Beilke, 1979) has suggested that the rate of transport in the aqueous phase also was enhanced by the use of the fans. However, neither the magnitude of systematic error in the rate constant (k/k') due to aqueous-phase diffusion limitation nor the supposed decrease in the magnitude of this error resulting from the use of the fans was quantitatively addressed by those authors. Since this

error may, as we have shown, be as great as an order of magnitude, one cannot lightly dismiss it by qualitative arguments as Beilke (1979) has recently attempted to do.

Before leaving the study of Barrie and Georgii, it is of interest to address the possibility of limitation to the rate of reaction due to the finite diffusion rate of O_2 . To this end we have evaluated the apparent diffusio-reactive parameter for O_2 , q'_O , which is related to that for S(IV) by Equation (44) of SF

$$q'_O = q'_S(D_{S(a)}\eta H_{SO_2}p_{SO_2}/2D_{O_2(a)}H_{O_2}p_{O_2})^{1/2}.$$

Here we have used $H_{O_2} = 1.27 \times 10^{-3} \text{ M atm}^{-1}$ (Loomis, 1928) and $D_{O_2(a)} = 2.3 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ (Himmelblau, 1964). The resulting values of q'_O are all less than unity, indicating that O_2 diffusion limitation was not appreciable under the conditions of these measurements.

Analysis of van den Heuvel and Mason (1963)

As a second example, we consider the study of van den Heuvel and Mason (1963). These investigators carried out experiments in which water droplets (0.05–0.25 mm radius) suspended on a grid of fibers were exposed to a stirred air stream containing 5 ppm each of SO_2 and NH_3 . After an exposure period of 7.5–30 min, the amount of S(IV) oxidized to S(VI) was determined. As noted in Section 2, there has been protracted discussion in the literature about whether the conversion rate in the study of van den Heuvel and Mason (1963) was limited by the intrinsic chemical rate or by aqueous-phase diffusion. It is therefore of interest to see what insights into that study may be gained from application of the theoretical framework developed by SF.

In Table 2 are listed data derived from Fig. 4 of van den Heuvel and Mason (1963) describing the rate of uptake for the range of droplet sizes examined. \bar{R} was calculated from the mass of $(NH_4)_2SO_4$ at 7.5 min; as noted by the original investigators, the data for the several measurement times indicated that within the scatter of the data \bar{R} was roughly independent of time over the time interval studied. On the other hand, inspection of \bar{R} as a function of drop size shows a systematic decrease (by more than a factor of 2) with increasing drop radius, which suggests diffusion limitation. The approximate inverse relationship of \bar{R} with droplet radius has led to the inference of aqueous-phase diffusion limitation (van den Heuvel and Mason, 1963; Carabine, 1972).

We proceed first to consider aqueous phase diffusion. Examination of Table 2 shows that the characteristic aqueous diffusion time $\tau_{d.a.}$ is much less than the contact times employed and is as well much less than the apparent aqueous-phase characteristic reaction time $\tau_{c.a.}$. These two comparisons *entirely rule out the possibility of aqueous phase diffusion limitation by S(IV) species*. We also examine O_2 -diffusion limitation. Evaluation of q'_O shows that this quantity does not exceed 1.11. Hence limitation to the rate of uptake

as a consequence of a non-uniform steady-state O_2 profile in the aqueous phase cannot be greater than 10%.

We now address possible gas-phase diffusion. We shall treat this problem initially by considering mass transport to occur only by molecular diffusion, which provides an upper limit to the magnitude of this effect. The characteristic time for gas-phase diffusion $\tau_{d.g.}$ is seen to be much shorter than the exposure times. Comparison of $\tau_{d.g.}$ with $\tau_{c.g.}$ shows that these quantities are comparable and thus suggests the possibility of significant gas-phase non-uniformity. However, evaluation of $G_\infty/G(a)$ shows that the magnitude of steady-state gas-phase diffusion limitation is at most 22% and varies only some 17% over the range of droplet sizes studied. Any turbulent mixing brought about by gas-stirring would only serve to decrease this variation. Thus it appears that a non-uniform steady-state gas-phase concentration profile can be ruled out as the cause of the diffusion limitation in this experiment.

A major difference between the experimental conditions of van den Heuvel and Mason (1963) and those of Barrie and Georgii (1976) is the presence of 5 ppm of NH_3 in addition to the reagent SO_2 . This ammonia provides a high degree of buffering capacity, which in turn results in a great increase in the solubility of sulfur-IV— $\eta H = 5.4 \times 10^4 \text{ M atm}^{-1}$ in contrast to (4–50) M atm^{-1} in Barrie and Georgii. A consequence of this increased solubility is that the atmosphere surrounding each droplet must supply a large amount of SO_2 to the drop before the steady state condition can be reached. For gas-phase mass transport by molecular diffusion, the characteristic time of this process in the absence of diffusion limitation is $\tau_{reag.}$. This quantity is given in Table 2 for the range of drop sizes employed, as evaluated for $[SO_4^{2-}] = 0$; (examination of $\tau_{reag.}$ as a function of $[SO_4^{2-}]$ showed negligible change for sulfate concentrations achieved within the duration of the experiment). The values of $\tau_{reag.}$ (220–2200 s) increase strongly with increasing drop size over the size range studied and are comparable to the contact times employed, 450–1800 s. Consequently, one may reasonably infer that the steady-state condition was not fulfilled under the conditions of this experiment. The extent of departure from steady state cannot be further addressed quantitatively because, as we have noted, the investigators employed stirring to enhance gas-phase mixing. However, because of the increase in $\tau_{reag.}$ with increasing droplet diameter, we would expect that the effect of departure from the steady-state reagent concentration would be greatest for the largest droplets. This would account at least qualitatively for the observed decrease in \bar{R} with increasing drop radius. These considerations, as well as the conditions of spatial and temporal uniformity established above, lead us to conclude that the observed diffusion limitation in the study of van den Heuvel and Mason (1963) was due to the failure to achieve steady-state reagent concentration as limited

Table 2. Characteristic times and related quantities in the experiment of van den Heuvel and Mason (1963)

a (cm)	$\tau_{d.a.}$ (s)	$\tau_{d.g.}$ (s)	τ_{reag} (s)	$C(7.5 \text{ min})^\dagger$ (M)	\bar{R} (M s ⁻¹)	$\tau_{c.a.}$ (s)	$\tau_{c.g.}$ (s)	q'_S	$G_\infty/G(a)$	q'_O
0.79(-2)	0.35	5.0(-5)	2.2(2)	2.5(-2)	5.6(-5)	4.8(3)	3.7(-3)	2.7(-2)	1.06	0.55
1.12(-2)	0.71	1.0(-4)	4.4(2)	2.2(-2)	4.8(-5)	5.6(3)	4.3(-3)	3.5(-2)	1.11	0.73
1.58(-2)	1.4	2.0(-4)	8.7(2)	1.5(-2)	3.4(-5)	8.0(3)	6.0(-3)	4.2(-2)	1.16	0.86
1.94(-2)	2.1	3.0(-4)	1.3(3)	1.2(-2)	2.8(-5)	9.8(3)	7.4(-3)	4.6(-2)	1.20	0.95
2.24(-2)	2.8	4.0(-4)	1.7(3)	1.1(-2)	2.5(-5)	1.1(4)	8.3(-3)	5.0(-2)	1.25	1.04
2.50(-2)	3.5	5.0(-4)	2.2(3)	1.0(-2)	2.2(-5)	1.2(4)	9.3(-3)	5.4(-2)	1.29	1.11

* The pH and S(IV) solubility were calculated for the following equilibria being satisfied at 25°C:

$$[\text{SO}_{2(\text{aq})}] = H_{\text{SO}_2} p_{\text{SO}_2},$$

$$[\text{NH}_{3(\text{aq})}] = H_{\text{NH}_3} p_{\text{NH}_3},$$

$$\frac{[\text{HSO}_3^-][\text{H}^+]}{[\text{SO}_{2(\text{aq})}]} = K_{a1},$$

$$\frac{[\text{SO}_3^{2-}][\text{H}^+]}{[\text{HSO}_3^-]} = K_{a2},$$

$$\frac{[\text{NH}_{3(\text{aq})}][\text{H}^+]}{[\text{NH}_4^+]} = \frac{K_w}{K_b}$$

subject to the electroneutrality constraint: $[\text{NH}_4^+] = [\text{HSO}_3^-] + 2[\text{SO}_3^{2-}]$. For K_{a1} , K_{a2} and H_{SO_2} see Schwartz and Freiberg (1981). For H_{NH_3} the value 75.3 M atm^{-1} (Hales and Drewes, 1979) was employed.

† $(\text{NH}_4)_2\text{SO}_4$ concentration after 7.5 min exposure, calculated from reported mass and droplet radius.

$$p_{\text{SO}_2} = 5 \times 10^{-6} \text{ atm}$$

$$p_{\text{NH}_3} = 5 \times 10^{-6} \text{ atm}$$

$$\text{pH} = 6.35^*$$

$$[\text{S(IV)}]_* = 0.27 \text{ M}^*$$

$$\eta \text{HRT} = 1.36 \times 10^6^*$$

$$\tau_{a1} = 3 \times 10^{-6} \text{ s}$$

$$\tau_{a2} = 6 \times 10^{-5} \text{ s}$$

$$\tau_{\text{phase}} = 0.5 \text{ s}$$

by gas-phase diffusion.

The data of van den Heuvel and Mason (1963) were subsequently utilized by Scott and Hobbs (1967) to derive a rate constant for the oxidation process. The latter authors assumed a mechanism first order in $[\text{SO}_3^{2-}]$, evaluating the $[\text{SO}_3^{2-}]$ concentration from the known aqueous-phase equilibria (Table 2), under the assumption that the dissolved S(IV) was in equilibrium with gas-phase SO_2 . As we have shown, the equilibrium S(IV) concentration was not established in the contact times employed, and consequently the value of $[\text{SO}_3^{2-}]$ used by Scott and Hobbs (1967) was considerably greater than the actual value. In turn, the rate constant derived was correspondingly smaller than the true value.

The above examples illustrate the pitfalls that may be encountered in experimental investigation of the reactions of gases in droplets, and serve also to show how the theoretical framework developed by SF can be used to systematically address potential mass-transport limitation to the rate of reaction in such studies. It is hoped that application of such analysis in the future will prevent the type of controversies that were described in Section 2 of this paper.

4. APPLICATION TO THE AMBIENT ATMOSPHERE

The theoretical framework that has been developed may be applied to examination of mass-transport limitation to the rate of chemical reaction in clouds or fogs. Here it is useful to consider not only the aqueous phase rate R but also the rate referred to gas-phase SO_2 . We introduce the quantity ρ , the fraction of gas-phase SO_2 that reacts per unit time

$$\rho = L\bar{R}/[\text{SO}_{2(g)}] = LRT\bar{R}/p_{\text{SO}_2}, \quad (1)$$

where L is the volume-fraction liquid water content (e.g. $L = 10^{-6}$ corresponds to $10^{-6} \ell_{\text{liq}} \ell^{-1}$ or 1 g liquid water m^{-3}). The fractional rate is seen to have the same units as are commonly employed to express gas-phase oxidation rates (e.g. $1\% \text{ h}^{-1} = 2.8 \times 10^{-6} \text{ s}^{-1}$), facilitating comparison.

Provided that there is no mass-transport limitation to the reaction rate

$$R = k[\text{S(IV)}]_* = k\eta H p_{\text{SO}_2}, \quad (2)$$

and hence

$$\rho = kL\eta HRT. \quad (3)$$

Assuming no mass-transport limitation we may use Equation (3) to evaluate ρ for representative atmospheric conditions. The resulting values of ρ are given in Fig. 1 as a function of pH for various values of k . The data of Barrie and Georgii (Table 1, pH 2.1–3.3) suggest values of k ranging from $7 \times 10^{-3} \text{ s}^{-1}$ at low catalyst concentrations (10^{-5} M MnCl_2) to 1.3 s^{-1} for higher concentrations of mixed catalysts ($10^{-4} \text{ M MnCl}_2 + 10^{-4} \text{ M FeCl}_2$). Values of k for SO_2 oxidation by representative concentrations of O_3

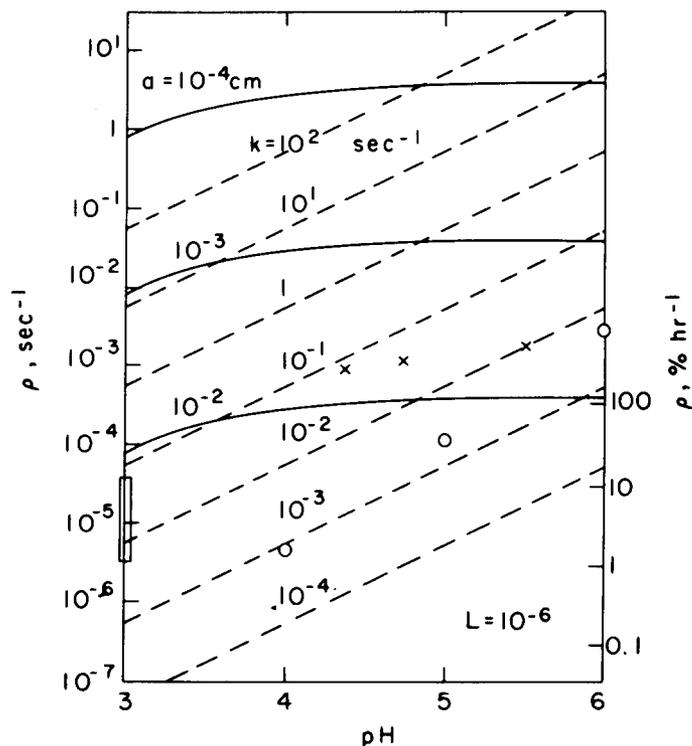


Fig. 1. Correspondence between k , the first-order rate constant for oxidation of S(IV) and ρ , the fractional removal rate of gas-phase SO_2 , for a liquid water content $L = 10^{-6} \ell_{\text{liq}} \ell^{-1}$ (1 g m^{-3}), as a function of pH. Dashed lines give correspondence in absence of diffusion limitation. Solid curves show onset of diffusion limitation (10% limitation) as a function of droplet radius. For other values of liquid water content L' , multiply ordinate scale labels by the factor (L'/L) . Also shown are rate constants for SO_2 oxidation derived from data of Barrie and Georgii (1976) as given in Table 1 (\square), and from data of Penkett *et al.* (1979) for oxidation by 50 ppb O_3 (\circ) and by $4 \times 10^{-4} \text{ M H}_2\text{O}_2$ (\times). All data for 25°C .

(50 ppb) or H_2O_2 (1 ppb) in the range $8 \times 10^{-4} - 6 \times 10^{-2} \text{ s}^{-1}$ have been given by Penkett *et al.* (1979). The conversion rates given by Equation (3) with values of k in this range are seen to be extremely high—cf. average gas-phase oxidation rates of the order of $0.2\% \text{ h}^{-1}$ and peak, polluted-atmosphere rates of $4\% \text{ h}^{-1}$ (Calvert *et al.*, 1978). It should be noted that the ordinate scale of Fig. 1 is given for $L = 10^{-6}$ (i.e. 1 g liquid water m^{-3}), at the high end of the range of observed cloud water content (Pruppacher and Klett, 1978). However, even for L an order of magnitude lower, the fractional reaction rate of SO_2 for these values of k remains quite high compared to gas-phase oxidation rates.

We have noted that Equations (2) and (3) are valid only in the absence of mass-transport limitation. In order to examine the possibility of mass-transport limitation we also give in Fig. 1 the values of ρ at which mass-transport limitation becomes appreciable (10%) as evaluated from Fig. 8 of SF for several values of droplet radius a . As anticipated, the onset of mass-transport limitation occurs at a lower rate for larger droplets. However, even for droplets of radius 10^{-3} cm ($10 \mu\text{m}$), towards the high end of the cloud droplet spectrum (Pruppacher and Klett, 1978), mass transport limitation is appreciable only for values of k greater

than 0.1 s^{-1} (pH 6) to 10 s^{-1} (pH 3). This bound on k encompasses the range indicated in Fig. 1 for SO₂ oxidation on the basis of laboratory measurements of k . It should be noted however that the rate constants for oxidation of SO₂ by O₃ and H₂O₂ scale linearly with oxidant concentration. Thus for O₃ = 500 ppb, mass transport limitation of SO₂ oxidation in a pH 6 droplet would become appreciable for droplet radius of 10 μm. Nevertheless, it appears that under most conditions mass transport limitation would not be appreciable for SO₂ oxidation in clouds or fogs.

With respect to droplets having radii greater than a few tens of micrometers, inspection of Fig. 1 suggests that mass transport limitation to the rate of uptake might be significant. However, such droplets would exhibit significant fall velocities (Pruppacher and Klett, 1978) that would induce enhanced mixing in both the gas and aqueous phases. This situation, which has been treated previously by Hales (1972), falls outside the scope of the present paper.

5. SUMMARY AND CONCLUSIONS

The aqueous-phase oxidation of SO₂, like any other gas-liquid reaction, inevitably involves competition between mass transport and chemical reaction. From our brief review of the literature we have seen that the development of a quantitative understanding of this reaction system has been hindered by an inadequate appreciation of the effect of the finite rate of mass transport upon the reaction rate, which may exert a controlling influence not only upon studies in bulk solutions but also upon studies carried out with small droplets.

In the present article we have applied the conceptual framework of Schwartz and Freiberg (1981), treating mass transport limitation to the rate of oxidation of SO₂ in aqueous droplet, to an examination of two laboratory investigations. As a consequence of aqueous-phase mass-transport limitation the reaction rates reported by Barrie and Georgii (1976) may be 20% to an order of magnitude smaller than the intrinsic rates. Significant gas-phase limitation may have been present as well. Because of the high solubility of S(IV) in the presence of NH₃, the contact times employed in the experiment of van den Heuvel and Mason (1963) were insufficient for the equilibrium reagent concentration to have been established. Thus the rates derived by Scott and Hobbs (1967) from the data of that study are considerably smaller than the intrinsic rates.

Consideration was given also to mass transport limitation to the oxidation of SO₂ by clouds and fogs. It appears that mass transport limitation is not appreciable under ordinary ambient conditions, but may become appreciable at very high oxidation rates, e.g. at high ozone or H₂O₂ concentrations.

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