

# MASS-TRANSPORT LIMITATION TO THE RATE OF REACTION OF GASES IN LIQUID DROPLETS: APPLICATION TO OXIDATION OF SO<sub>2</sub> IN AQUEOUS SOLUTIONS\*

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**Abstract**—Aqueous-phase oxidation of SO<sub>2</sub> occurs via a sequence of steps consisting of gas-phase diffusion, mass transfer at the gas-water interface, hydrolysis and ionization of the dissolved sulfur-IV, aqueous-phase diffusion, and oxidation reaction. Expressions are given for the characteristic times of these several processes for reaction in aqueous droplets. Readily applicable criteria are developed in terms of these characteristic times to delimit the conditions, in the laboratory or in the ambient atmosphere, under which the rate of reaction in an aqueous droplet is equal to the intrinsic oxidation rate or is restricted by the finite rates of the several other processes. Under most conditions of concern in the ambient atmosphere, or in laboratory simulation of these conditions, the characteristic times of hydrolysis and ionization are sufficiently short compared to that of aqueous-phase reaction that the several dissolved sulfur-IV species may be considered to be a single pool of equilibrated reactant species. Similarly, the S(IV) solubility equilibria at the gas-water interface may also be considered to be achieved on a time scale that is short compared to that of aqueous-phase reaction, except perhaps at high pH (pH > 7) where the characteristic time of this process becomes long (~10 sec at 25°C) because of the high solubility of S(IV).

A more detailed treatment of the problem of simultaneous diffusion and reaction establishes the domain of applicability of the steady-state assumption for reaction in aqueous droplets. Within the steady state approximation, we examine the magnitude of limitation to the overall rate of reaction resulting from the finite rate of mass transport in the gas and aqueous phases and from the finite rate of achieving the solubility equilibrium at the interface. Expressions are presented that permit this treatment to be readily applied to laboratory kinetic data.

The foregoing treatment also permits examination of the conditions under which limitation to the overall rate of reaction is controlled by one or another of the above mechanisms. For gas- and aqueous-phase mass transport by molecular diffusion it is found (again for 25°C) that gas-phase mass transport is more controlling than aqueous-phase mass transport for pH > 3.3, and that the onset of departure from the solubility equilibrium at the phase interface is more controlling than gas-phase diffusion only for very small droplets (radius < 0.16 μm). For SO<sub>2</sub> oxidation by atmospheric O<sub>2</sub>, aqueous-phase diffusion of O<sub>2</sub> is more controlling than gas-phase diffusion of SO<sub>2</sub> only for quite high SO<sub>2</sub> partial pressure ( $p_{\text{SO}_2} > 10$  ppm).

## NOMENCLATURE

<i>A</i>	Aqueous-phase reagent concentration (M)	<i>k</i>	First-order rate coefficient (s <sup>-1</sup> )
<i>G</i>	Gas-phase reagent concentration (M)	<i>t</i>	Time variable (s)
<i>R</i>	Reaction rate (M sec <sup>-1</sup> )	<i>p</i>	Gas partial pressure (atm)
<i>H</i>	Coefficient of physical (Henry's law) solubility (M atm <sup>-1</sup> )	$\bar{v}$	Mean molecular speed (cm s <sup>-1</sup> )
<i>F</i>	Flux of material into droplet (mol s <sup>-1</sup> )	<i>q</i>	Dimensionless parameter describing reaction and aqueous-phase diffusion, Equation (15).
<i>M</i>	Amount of material in droplet (mol)	<i>g</i>	Dimensionless parameter describing reaction and gas-phase diffusion, Equation (33).
<i>D<sub>a</sub></i>	Diffusion coefficient, aqueous phase (cm <sup>2</sup> s <sup>-1</sup> )	<i>y</i>	<i>kt</i>
<i>D<sub>g</sub></i>	Diffusion coefficient, gas phase (cm <sup>2</sup> s <sup>-1</sup> )	<i>z</i>	<i>r/a</i>
<i>R</i>	Universal gas constant (ℓ atm/mol K)	<i>η</i>	Solubility factor, dimensionless, Equation (2).
<i>T</i>	Temperature (K)	<i>ξ</i>	Sticking coefficient, dimensionless, Equation (6).
<i>a</i>	Drop radius (cm)	<i>σ</i>	Collision rate (mol cm <sup>-2</sup> s <sup>-1</sup> )
<i>r</i>	Radius variable (cm)	<i>τ</i>	Characteristic time (s) representative of indicated process, denoted by the following subscripts: c.a. Chemical reaction, referred to aqueous-phase concentration c.g. Chemical reaction, referred to gas-phase concentration d.a. Diffusion, aqueous phase d.g. Diffusion, gas phase phase Establishing phase equilibrium at air-water interface

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a1	Hydrolysis of SO <sub>2</sub> and first ionization of sulfurous acid
a2	Second ionization of sulfurous acid
reag	Establishing equilibrium aqueous-phase reagent concentration.
$\bar{R}, \bar{A}$	Average over droplet volume
$R_{ss}, A_{ss}$	Steady-state values
$R_{max}$	Gas-phase diffusion limited maximum rate, Equation (30)
$G(a), A_*$	Values at surface of droplet
$G_x, A_x$	Equilibrium values referred to bulk gas-phase concentration
$k', q'$	Apparent values based on measured $\bar{R}$ .

## 1. INTRODUCTION

There is now considerable evidence from both laboratory investigations and field studies showing the importance of heterogeneous reactions of SO<sub>2</sub> in the atmospheric formation of aerosol sulfate (ISSA, 1978). Such heterogeneous oxidation may be catalyzed by solid surfaces (Liberti *et al.*, 1978; Chang *et al.*, 1978) or may take place in aqueous solutions (clouds or aerosols) (Beilke and Gravenhorst, 1978; Hegg and Hobbs, 1978) by transition-metal catalyzed reaction (Barrie and Georgii, 1976) or by reaction with such oxidants as O<sub>3</sub> or H<sub>2</sub>O<sub>2</sub> (Penkett *et al.*, 1979; Larson *et al.*, 1978). Despite a corpus of research extending for some five decades, the present quantitative understanding of these heterogeneous reactions remains rather primitive [Freiberg and Schwartz (1980), accompanying paper (FS)]. One reason for this is the failure properly to take into account the influence upon the rate of reaction of the finite rate of mass transport within each phase and across phase boundaries. This factor pertains both to the interpretation of relevant laboratory studies and to the description of the rates of these processes in the ambient atmosphere.

This paper addresses the role of mass transport in the oxidation of SO<sub>2</sub> to sulfate in aqueous droplets. We first enumerate the several steps that occur as components of the overall process and present expressions by which the time quantities characteristic of these steps may be calculated. From comparison of these characteristic times it may readily be determined

whether or not mass-transport limitation significantly affects the rate of the overall process. Then, after setting out the basic mathematical equations which describe mass transport coupled to aqueous-phase reaction, we develop a theoretical framework that is suitable for determining the magnitude of mass-transport limitation to the rate of oxidation of SO<sub>2</sub> in aqueous droplets in laboratory experiments or in the ambient atmosphere.

The methodology developed in the present paper can be utilized for design of laboratory investigations of SO<sub>2</sub> oxidation in droplets and for the analysis of previous such studies from the perspective of the influence of mass transport upon observed reaction rates. In the accompanying paper (FS) we review the existing literature from this perspective. We then apply the present methodology to an examination of the cause and magnitude of mass-transport limitation in two such studies (Barrie and Georgii, 1976; and van den Heuvel and Mason, 1963). Mass-transport limitation to the aqueous-phase oxidation of SO<sub>2</sub> in clouds or fogs is also addressed.

The sequence of steps that occurs when SO<sub>2</sub> reacts with O<sub>2</sub> to form sulfate in an aqueous droplet (either in the laboratory or in the atmosphere) is depicted in Fig. 1 and consists of the following processes:

- Transport of SO<sub>2</sub> (and O<sub>2</sub>) within the gas phase to the gas-liquid interface.
- Establishment of local solubility equilibria (Henry's law) at the interface.
- Hydrolysis of SO<sub>2</sub> and partial ionization to HSO<sub>3</sub><sup>-</sup> and SO<sub>3</sub><sup>2-</sup>.
- Transport of these S(IV) species, H<sup>+</sup>, and O<sub>2</sub> within the aqueous phase.
- Oxidation of the S(IV) precursor(s) to S(VI).
- Subsequent adjustment of the ionization equilibria.
- Mass transport resulting from the concentration gradients introduced by steps (e) and (f).

A principal objective of laboratory studies has been the determination of the intrinsic rate of oxidation  $d[S(VI)]/dt$ , step (e), since the remaining processes are considered to be adequately described theoretically

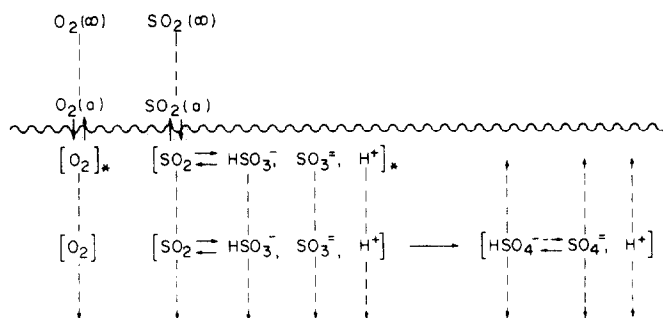


Fig. 1. Pictorial representation of processes occurring in the aqueous-phase oxidation of SO<sub>2</sub>.

and/or to be sufficiently fast under atmospheric conditions as to exert negligible influence on the rate of the overall process. However, insofar as laboratory studies employ conditions that depart from atmospheric conditions, the remaining processes may exert a considerable influence upon the measured rate. This applies particularly to studies with bulk solutions for which there has been recurrent concern (as discussed in FS) as to the adequacy of the mixing processes relative to both sulfur-IV and oxygen. The desire to minimize the effects of mass transport and to more closely simulate reactions in atmospheric aerosols has motivated experiments employing liquid droplets with both  $\text{SO}_2$  and  $\text{O}_2$  as gaseous reagents. However, even for these studies it has not been clear whether the measured rate of reaction is equal to the intrinsic oxidation rate or is restricted by mass transport, and indeed there are no accepted and readily applicable criteria by which to test for the presence or absence of mass-transport limitation. This situation has led to the extended discussion that is reviewed by FS. In order to develop such criteria we set out the characteristic times of the several steps that comprise the overall process, under the intuitive supposition (as confirmed in Section 3) that mass-transport limitation will be absent when the characteristic time of the aqueous-phase reaction greatly exceeds each of the several other characteristic times.

## 2. THE CHARACTERISTIC TIMES

In this section we present mathematical expressions for the characteristic times associated with the several processes outlined earlier, considered one at a time. Evaluation and comparison of these characteristic times permits an initial scoping of a particular set of experimental conditions that in turn permits an assessment of whether the rate of uptake in a situation of interest is limited by the rate of chemical reaction, as desired, or whether more detailed treatment is required. Examination of these characteristic times is thus seen to be a useful point of departure in considering mass transport limitation to the overall rate of reaction.

In considering the characteristic times it is useful to distinguish those steps that are intrinsic to a particular chemical system (i.e. establishment of the ionization equilibria and the oxidation step) from those which

describe the transport of material within and between the two phases. The latter processes serve to maintain the concentrations of the reagent species in the face of depletion of these concentrations by occurrence of reaction. The rates of these processes depend upon the extent of physical contact between the two phases (e.g. droplet size), upon the rates of molecular diffusion in the two phases, and upon any mechanical mixing that may be applied. The rates of the intrinsic processes are independent of the physical situation, but would be expected to exhibit dependence upon the chemical properties of the system (e.g. pH and the concentrations of gaseous and aqueous species) as well as upon temperature.

We first consider the characteristic time associated with the oxidation reaction. Since the oxidation of sulfur-IV is essentially irreversible, the characteristic time of this process is that of the forward reaction. Under the assumption, justified below, that interconversion between the sulfur-IV species is fast compared to oxidation, then the effective time constant  $\tau_{\text{c.a.}}$  associated with chemical reaction of aqueous sulfur-IV species is given by

$$\tau_{\text{c.a.}}^{-1} = \frac{1}{[\text{S(IV)}]} \frac{d[\text{S(IV)}]}{dt}, \quad (1)$$

where  $[\text{S(IV)}]$  denotes the total aqueous concentration of sulfur-IV species,  $[\text{S(IV)}] = [\text{SO}_{2(\text{aq})}] + [\text{HSO}_3^-] + [\text{SO}_3^{2-}]$ , and  $-d[\text{S(IV)}]/dt$  denotes the rate of oxidation. For S(IV) in equilibrium with gaseous  $\text{SO}_2$

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

where  $\eta$ , the ratio of dissolved S(IV) to dissolved  $\text{SO}_2$ , is given by

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

and where  $H$  is the solubility (Henry's law) coefficient of  $\text{SO}_2$ .  $K_{a1}$  and  $K_{a2}$  are the first and second ionization constants of sulfurous acid. Numerical values of  $H$ ,  $K_{a1}$ , and  $K_{a2}$  are given in Table 1. The solubility of  $\text{SO}_2$  increases strongly with increasing pH as indicated in Fig. 2. For a reaction first-order in sulfur-IV,  $d[\text{S(IV)}]/dt = -k[\text{S(IV)}]$  and

$$\tau_{\text{c.a.}} = k^{-1}. \quad (1a)$$

The characteristic time of reaction, the determination of which is the objective of laboratory experimentation, must be compared to the several other

Table 1. Solubility coefficient, acid dissociation constants and diffusion coefficients of sulfur-IV\*

Reaction or process	Equilibrium constant or coefficient	Reference
$\text{SO}_{2(\text{g})} = \text{SO}_{2(\text{aq})}$	$H = 1.26 \text{ M atm}^{-1}$	Johnstone and Leppla (1934)
$\text{SO}_{2(\text{aq})} + \text{H}_2\text{O} = \text{H}^+ + \text{HSO}_3^-$	$K_{a1} = 1.74 \times 10^{-2} \text{ M}$	Sillén (1964)
$\text{HSO}_3^- = \text{H}^+ + \text{SO}_3^{2-}$	$K_{a2} = 6.24 \times 10^{-8} \text{ M}$	Sillén (1964)
Aqueous diffusion	$D_a = 1.8 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$	Himmelblau (1964)
Gaseous diffusion	$D_g = 0.126 \text{ cm}^2 \text{ s}^{-1}$	Andrew (1955)

\* Values are given for 25°C.

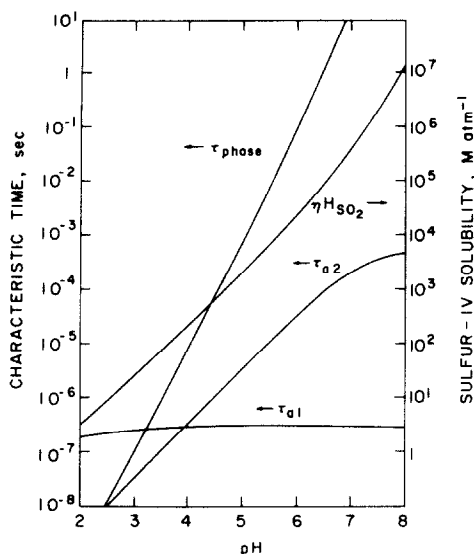
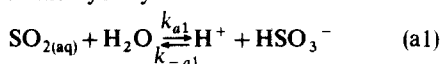


Fig. 2. pH dependence of characteristic times of establishing hydrolysis and first ionization, second-ionization, and phase equilibria of  $\text{SO}_2$  (left-hand scale) and of sulfur-IV solubility (right-hand scale), evaluated for 25°C.

characteristic times to be developed below. In particular, it will be shown below that  $\tau_{\text{c.a.}}$  must substantially exceed the characteristic time associated with aqueous diffusion in order that the rate of reaction not be diminished by the finite rate of aqueous-phase diffusion.

The relaxation times associated with the  $\text{SO}_2$  hydrolysis and ionization equilibria have been examined by Eigen *et al.* (1961) and have been addressed in the present context by Beilke and Lamb (1975), and Carmichael and Peters (1979). The first-order rate constant for the hydrolysis reaction

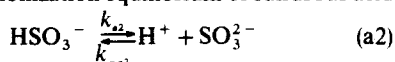


is  $k_{a1} = 3.4 \times 10^6 \text{ s}^{-1}$  at 25°C, and for the reverse reaction  $k_{-a1} = 2.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ . The relaxation time is evaluated as

$$\tau_{a1}^{-1} = k_{a1} + k_{-a1}[\text{H}^+] + k_{-a1}[\text{HSO}_3^-]. \quad (3)$$

It is seen that  $k_{a1}$  is the dominant term in Equation (3) for  $\text{H}^+$  and  $\text{HSO}_3^-$  concentrations of concern. The resulting value for the relaxation time is  $\tau_{a1} \approx 3 \times 10^{-7} \text{ s}$  over the entire pH range of concern, as indicated in Fig. 2.

The second ionization equilibrium of sulfurous acid



is important at higher values of pH. The relaxation time for this equilibrium may be estimated on the assumption that the protonation reaction is diffusion limited (Eigen *et al.*, 1964), i.e.  $k_{-a2} \gtrsim 3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ . From the acid dissociation constant  $K_{a2}$ , we estimate  $k_{a2} \gtrsim 1.9 \times 10^3 \text{ s}^{-1}$ . The resultant estimate for  $\tau_{a2}$  is given by

$$\tau_{a2}^{-1} = k_{a2} + K_{-a2}[\text{H}^+] + k_{-a2}[\text{SO}_3^{2-}], \quad (4)$$

and is shown in Fig. 2, in the limit of low  $[\text{SO}_3^{2-}]$ .

As we shall see below, these relaxation rates are rapid compared to the rate of air oxidation of sulfur-IV species. Consequently we must consider the several aqueous sulfur-IV species to be in equilibrium and treat them as a single pool of diffusing and reacting species.

The time required for phase equilibrium to be established locally at a gas-liquid interface in the absence of reaction has been considered by Danckwerts (1949, 1970) in terms of the kinetic theory of gases. The time constant characteristic of this process is given by

$$\tau_{\text{phase}} = D_a \left( \frac{4HRT}{\bar{v}\zeta} \right)^2, \quad (5)$$

where  $D_a$  is the aqueous-phase diffusion coefficient of the dissolved species ( $\text{cm}^2 \text{ s}^{-1}$ ),  $R$  is the universal gas constant ( $\text{atm M}^{-1} \text{ K}^{-1}$ ),  $T$  is the absolute temperature,  $\bar{v}$  is the average speed of the gas-phase molecule ( $\text{cm s}^{-1}$ ), and  $\zeta$  is a "sticking-coefficient" (dimensionless). Experimental work has indicated that the sticking coefficient is generally the order of unity, except in the presence of surfactants (Danckwerts, 1970). If this is the case for  $\text{SO}_2$  absorbing into water, then the time constant  $\tau_{\text{phase}}$  may be evaluated by setting  $\zeta = 1$ . For a gas such as  $\text{SO}_2$ , which undergoes rapid reversible hydrolysis and ionization, the Henry's law coefficient  $H$  in Equation (5) must be replaced by  $\eta H$ . In the case of  $\text{SO}_2$ , because of the pH dependence of  $\eta$  there is a corresponding strong increase of  $\tau_{\text{phase}}$  with increasing pH, as shown in Fig. 2.

Examination of Fig. 2 shows that  $\tau_{\text{phase}}$  greatly exceeds  $\tau_{a1}$  and  $\tau_{a2}$  over most of the pH range of concern. At high pH  $\tau_{\text{phase}}$  is quite appreciable (1 s at pH = 6.5) because of the high solubility of sulfur-IV at such high pH ( $[\text{S(IV)}]/p_{\text{SO}_2} = 9 \times 10^4 \text{ M atm}^{-1}$  at pH = 6.5). In fact, however,  $\tau_{\text{phase}}$  calculated by Equation (5) may be somewhat unrealistic at high pH since a constant pH is assumed, which would require a sufficient buffering capacity to maintain this pH in the face of the high sulfur-IV solubility.

With regard to the characteristic times of mixing within the two phases, we have noted above that these are not intrinsic properties of the system under investigation, but depend on the nature of the physical contact between the two phases. In the absence of mechanically or convectively induced mixing this mixing is achieved by molecular diffusion, for which process the characteristic time is readily calculable from theory. This characteristic time governs the approach of the concentration profile (in either gas or aqueous phase) to the steady-state (time-independent) profile (which may or may not be spatially uniform, as will be discussed below). For a spherical drop the characteristic diffusion times are given by

$$\tau_{\text{d.a.}} = a^2/\pi^2 D_a, \text{ aqueous phase}, \quad (6a)$$

$$\tau_{\text{d.g.}} = a^2/\pi^2 D_g, \text{ gas phase}, \quad (6b)$$

where  $a$  is the droplet radius and  $D_a$  and  $D_g$  are the

diffusion coefficients appropriate for the two phases (Crank, 1975). Since aqueous-phase diffusion coefficients are much smaller than gas-phase diffusion coefficients (typically by four orders of magnitude for 1 atm pressure) the characteristic diffusion times in the aqueous phase are correspondingly greater than in the gas phase, as indicated in Fig. 3. Consequently, the gas-phase concentration profile will accommodate rapidly to changes in the aqueous-phase concentration profile and may to good approximation be treated as a steady-state system as it "follows" the much more slowly varying aqueous-phase system.

An additional characteristic time, the significance of which is not obvious now, but which will be seen later to be important, is the characteristic time of chemical reaction relative to the gas-phase reagent concentration, defined as

$$\tau_{c.g.}^{-1} = \frac{1}{[SO_{2(\infty)}]} \frac{d[S(IV)]}{dt} \quad (7)$$

Here  $d[S(IV)]/dt$  represents the rate of reaction averaged over the droplet volume, and  $[SO_{2(\infty)}]$  represents the bulk gas-phase concentration. As will be shown later,  $\tau_{c.g.}$  must substantially exceed the characteristic time associated with gas-phase diffusion in order that the steady-state rate of reaction not be diminished by the finite rate by which gas-phase diffusion can replenish the reagent concentration. In this respect  $\tau_{c.g.}$  is analogous to the more obvious  $\tau_{c.a.}$  defined above. For a uniform aqueous-phase concentration  $[S(IV)] = \eta HRT [SO_{2(\infty)}]$ ,  $\tau_{c.g.}$  is related to  $\tau_{c.a.}$  by

$$\tau_{c.g.} = \tau_{c.a.}/\eta HRT. \quad (7a)$$

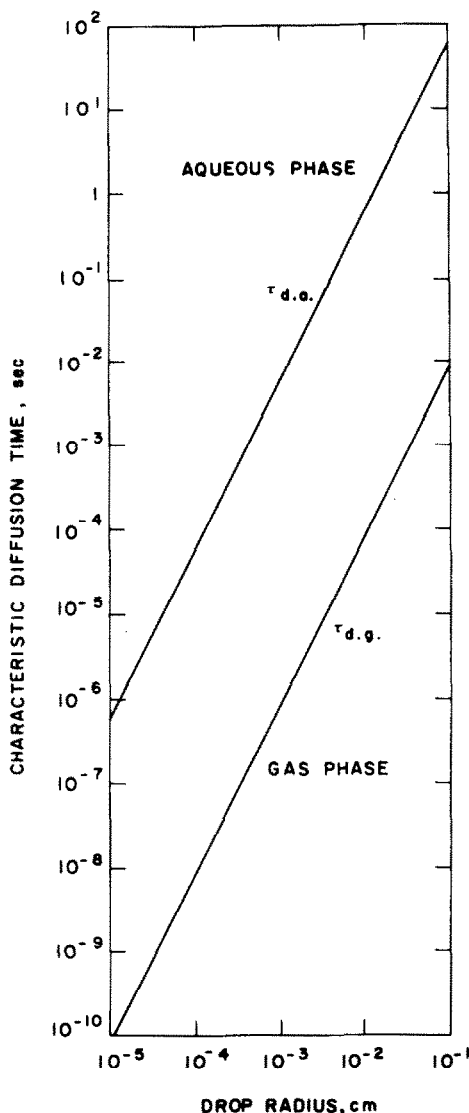


Fig. 3. Characteristic times for establishing steady-state concentration profiles by molecular diffusion, in gas and aqueous phases, as a function of radius for a spherical droplet. Diffusion coefficients were 0.126 and  $1.8 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ , respectively.

One final characteristic time, which we shall introduce below, addresses the time required for gas-phase diffusion to supply an amount of reagent to the droplet necessary to produce a concentration of dissolved reagent in equilibrium with the bulk gas-phase reagent concentration. As we shall see below, the characteristic time for this process,  $\tau_{\text{reag}}$ , is related to the characteristic time for gas-phase diffusion by

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

Because of the dependence of  $\eta$  upon pH,  $\tau_{\text{reag}}$  may become quite large at high pH even for small droplets.

We now consider the insights that may be gained from comparison of the characteristic times of reaction and mass transport. Much of the discussion that follows will address the interworking between chemical reaction and aqueous-phase diffusion. It is clear that if, as in the case in small droplets and/or slow rates of reaction, the characteristic time of aqueous-phase diffusion is much shorter than that of chemical reaction (i.e.  $\tau_{d.a.} \ll \tau_{c.a.}$ ) the rate of the overall process (i.e. the rate of sulfate production) will be controlled entirely by the rate of reaction. At the other extreme, if  $\tau_{d.a.} \gg \tau_{c.a.}$  (as is the case in large droplets and/or fast reactions), the rate of diffusion will significantly affect the rate of the overall process (though, as will be shown below, the overall rate never becomes entirely independent of the reaction rate). Additionally, of course, there is a "gray area" in which  $\tau_{d.a.}$  and  $\tau_{c.a.}$  are comparable in magnitude. In the first case ( $\tau_{d.a.} \ll \tau_{c.a.}$ ) the steady-state reactant concentration profile is uniform throughout the droplet, since diffusion is fast enough to replenish sulfur-IV as fast as reaction occurs. In the other two cases ( $\tau_{d.a.} \approx \tau_{c.a.}$  and  $\tau_{d.a.} \gg \tau_{c.a.}$ ) the steady-state reactant concentration profile will be non-uniform, decreasing as a function of distance from the droplet surface to the center, because of the inability of diffusion to keep up with the rate of reaction.

Regarding gas-phase diffusion, we shall show below that although  $\tau_{d.a.}$  is always much greater than  $\tau_{d.g.}$ , it is

nonetheless possible for the rate of sulfate formation to be restricted by the finite rate of gas-phase diffusion. This is because the concentration profile of  $\text{SO}_2$  in the gas phase depends on the ability of gas-phase diffusion to replenish  $\text{SO}_2$  that is removed by entering and reacting within the drop. As we have already said, we anticipate that there will be no gas-phase diffusion limitation for  $\tau_{d,g} \ll \tau_{c,g}$ , but that such limitation will be appreciable for  $\tau_{d,g} \gg \tau_{c,g}$ .

One further concern regards the assumption of phase equilibrium at the gas-water interface. Generally it has been assumed that Henry's law (as extended by the factor  $\eta$  to account for rapid aqueous-phase equilibria) holds locally at the interface, at least for times greatly in excess of  $\tau_{\text{phase}}$ . However, for a dissolved gas undergoing irreversible reaction, if this reaction is sufficiently fast, phase equilibrium may not be achieved, even in steady state. As is discussed below, the criterion for achieving this phase equilibrium in steady state is that  $\tau_{\text{phase}} \ll \tau_{c,a}$ .

The above qualitative discussion indicates (as confirmed below) that the rate of reaction in an aqueous droplet, as measured in the laboratory, is equal to the intrinsic rate, provided that mass transport limitation is absent, as indicated by comparison of the characteristic times. That discussion does not, however, give quantitative indication of the extent of mass-transport limitation when it is present, nor does it provide a means for analyzing experimental data to determine the extent of such limitation. For this quantitative discussion we turn to the mathematical treatment in the next section.

### 3. MODELS OF MASS TRANSPORT AND REACTION

We now proceed to consider quantitatively the rate of reaction in droplets under conditions where this rate may be significantly restricted by mass transport. We focus our attention first on mass transport and reaction within the droplet, assuming that the rate of uptake is not restricted by gas-phase diffusion. Afterwards we consider situations in which the rate of uptake may be restricted by gas-phase diffusion or by the finite rate of achieving phase equilibrium.

#### *Aqueous-phase diffusion and reaction*

In the model that is developed we examine the temporal and spatial evolution of the aqueous phase concentration of a reagent species, e.g.,  $\text{S(IV)}$ , after a spherical drop is suddenly exposed to a gaseous concentration of the reagent species that remains constant throughout the exposure. We also examine the temporal and spatial evolution of the total material (reactant plus product) in the droplet in this situation. The time and space dependence of the concentration of a species undergoing diffusion and irreversible reaction is described by

$$\frac{dA}{dt} = D_a \nabla^2 A - R(r, t) \quad (8)$$

Here  $A$  represents the concentration of the reactant, a function of time and position within the drop;  $D_a$  is the aqueous-phase diffusion coefficient of the reactant and  $R(r, t)$  represents the rate of reaction, a function of space  $r$  and time  $t$ . For a spherically symmetrical drop Equation (8) becomes

$$\frac{dA}{dt} = D_a \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial A}{\partial r} \right) - R(r, t), \quad (9)$$

where  $r$  is the radius variable. The constant gas-phase concentration is assumed to induce at the surface of the drop a constant solution-phase concentration  $A_*$  which corresponds to the equilibrium solubility of the gas in the liquid. These circumstances establish the following initial and boundary conditions

$$A(r, 0) = 0, \quad r < a, \quad (10a)$$

$$A(a, t) = A_*, \quad t \geq 0, \quad (10b)$$

where  $a$  is the radius of the drop and where the exposure of the drop to gas phase reagent starts at time  $t = 0$ .

The expression for the reaction rate depends on the kinetic mechanism. Johnstone and Coughanowr (1958) have treated the case of a zero-order reaction, whose rate is

$$R(r, t) = \begin{cases} k_0, & A > 0, \\ 0, & A = 0, \end{cases} \quad (11a)$$

and have interpreted their experimental data in terms of this model. We examine the case of an irreversible first-order reaction, whose rate

$$R(r, t) = kA. \quad (11b)$$

This partial differential equation also has been treated in detail (Danckwerts, 1951; Cadle and Robbins, 1960; Crank, 1975). Consequently, we restrict the present discussion largely to a statement of the results and application to the interpretation of experimental studies.

Solution of Equation (9) is conveniently achieved by considering first the solution to the steady-state equation, obtained by setting  $\frac{dA}{dt} = 0$ . Physically this solution is achieved at long times after the initial transient, resulting from the influx of reactant into the droplet, has decayed. This decay is quite rapid. As is shown in the Appendix, the rate of uptake into the drop exceeds the steady-state rate by no more than 7% at  $t = k^{-1}$  and 1.1% at  $t = 2k^{-1}$ . In the steady state condition the amount of dissolved reagent is constant, and thus the rate of uptake is equal to the rate of reaction. The steady state solution  $A_{ss}(r)$  is given by the solution of the ordinary differential equation

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dA_{ss}}{dr} \right) = \frac{k}{D_a} A_{ss}, \quad (12)$$

with boundary condition

$$A_{ss}(a) = A_*. \quad (13)$$

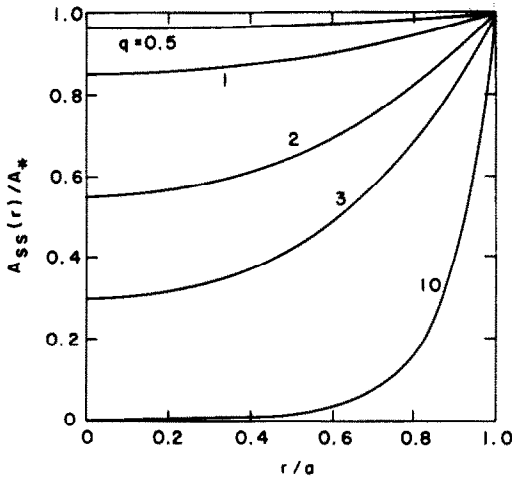


Fig. 4. Steady-state radial concentration profiles of concentration of a reactant species  $A(r)$ , relative to the concentration and the surface of the drop  $A_*$ , for a drop of radius  $a$ , for indicated values of the dimensionless parameter  $q = a(k/D_a)^{1/2}$ .

(In contrast to the reactant, the radial concentration profile of the product does not become constant at long times.) Much physical insight into this problem may be gained from consideration of the steady state limit.

The solution to Equation (12) with condition (13) is

$$A_{ss}(r) = A_* \frac{a \sinh(qr/a)}{r \sinh q}, \quad (14)$$

where we introduce the dimensionless parameter

$$q \equiv a(k/D_a)^{1/2}. \quad (15)$$

As we shall see, knowledge of the value of  $q$  characterizing a given physical system is fundamental to the understanding and description of the system. In order to enable appreciation of the role of the diffu-

reactive parameter  $q$  upon the steady-state concentration profiles within the drop, we show these profiles in Fig. 4 for several values of  $q$ . It is seen that at low values of  $q$ , the steady state reaction profile is nearly uniform. This reflects the rapidity of diffusion relative to reaction. However, for values of  $q$  of the order of unity and greater there is an appreciable depletion of  $A_{ss}$  towards the center of the drop, reflecting the inability of diffusion to restore the decrease in  $A_{ss}$  caused by chemical reaction. In other words, with increasing  $q$  there is decreasing penetration by  $A_{ss}$  from the surface of the drop into the interior. This effect is displayed also in Fig. 5, in which the concentration at the center of the drop

$$A_{ss}(0) = A_* \frac{q}{\sinh q}, \quad (16)$$

is given as a function of  $q$ .

More important than the dependence on  $q$  of the concentration at the center of the drop is the dependence on  $q$  of the average concentration  $\bar{A}_{ss}$ , since the rate of reaction averaged over the drop,  $\bar{R} = k\bar{A}$ , will at steady state be proportional to this average.  $\bar{A}_{ss}$  is evaluated as

$$\bar{A}_{ss} = (4\pi a^3/3)^{-1} \int_0^a 4\pi r^2 A_{ss}(r) dr. \quad (17)$$

Integration of  $A_{ss}(r)$  given in Equation (14) yields the result

$$\bar{A}_{ss}/A_* = 3 \left( \frac{\coth q}{q} - \frac{1}{q^2} \right). \quad (18)$$

This steady-state average concentration is also shown in Fig. 5 as a function of the parameter  $q$ . For  $q \geq 1$  the steady state average concentration  $\bar{A}_{ss}$  is seen to be significantly less than the equilibrium concentration  $A_*$ . The fall-off of  $\bar{A}_{ss}$  with increasing  $q$  is slower than that of the concentration at the center,  $A_{ss}(0)$ . This

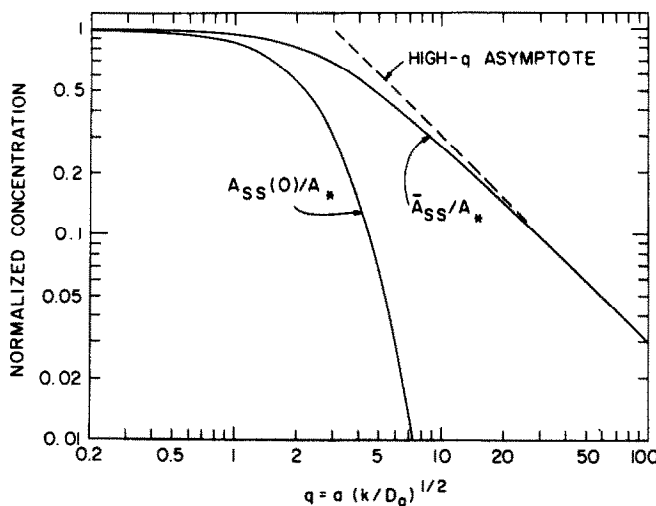


Fig. 5. Average concentration of reactant species  $\bar{A}$ , and concentration at the center of the drop  $A(0)$ , relative to the concentration at the surface of the drop  $A_*$ , at steady state, as a function of  $q$ .

slower fall-off reflects the large fraction of the volume of the drop that is "near" the surface. Several limiting approximations for  $\bar{A}_{ss}$  at low and high orders of  $q$ , will be useful in discussion which follows. For low values of  $q$  the ratio  $\bar{A}_{ss}/A_*$  is close to unity

$$\bar{A}_{ss}/A_* \approx 1, q \leq 1, \quad (18a)$$

taking the value 0.94 at  $q = 1$ . For moderately high values of  $q$ ,  $\bar{A}_{ss}$  is very closely approximated by

$$\bar{A}_{ss}/A_* = 3 \frac{q^{-1}}{q^2}, q \gtrsim 4. \quad (18b)$$

At high values of  $q$

$$\lim_{q \rightarrow \infty} \bar{A}_{ss}/A_* = 3 q^{-1}. \quad (18c)$$

It is instructive to compare the condition (18a) to the intuitive criterion developed above that  $\tau_{d,a} \ll \tau_{c,a}$  in order that the rate of uptake not be appreciably influenced by aqueous phase diffusion. From the definitions (1), (7) and (17) it may be seen that the condition  $q \leq 1$  is equivalent to  $\tau_{d,a} \leq 0.1 \tau_{c,a}$ , in agreement with the intuitive supposition.

Figure 5 may be used to address the dependence of the rate of reaction on drop radius, since  $\bar{R}_{ss}$ , the steady-state average rate of reaction per unit volume, is equal to  $k\bar{A}_{ss}$ . For constant  $k$  and  $D_a$ , it is seen that  $\bar{R}_{ss}$  is independent of  $a$  at low  $q$  but ultimately at large  $q$  decreases as  $a^{-1}$ . The expression (18) for  $\bar{A}_{ss}$  also permits consideration of  $\bar{R}_{ss}$  as the rate coefficient  $k$  is increased holding the drop radius and diffusion coefficient constant. (Such a dependence might be observed experimentally by varying the concentration of a dissolved catalyst.) In Fig. 6 is plotted a normalized rate of reaction  $\bar{R}_{ss}/(D_a A_* / a^2)$  as a function of the normalized rate constant  $k/(D_a / a^2)$  (which is equivalent to  $q^2$ ). Also shown in Fig. 6 are the asymptotes to this function for the low- $q$  [Equation (18a)] and

high- $q$  [Equation (18c)] limits. It is seen that at low values of  $k$  (and hence low values of  $q$ ) the average rate of reaction in the drop increases linearly as  $k$  is increased, since the reagent concentration within the drop remains uniform at the surface value  $A_*$ . As  $k$  continues to increase this linear relation ceases to hold, since diffusion can no longer maintain a uniform concentration profile, and the average concentration begins to decrease. However, it may be seen that the decrease in  $\bar{A}_{ss}$  with increasing  $k$  is always more than compensated for by the increase in  $k$ , so that the average reaction rate continues to increase with increasing  $k$ . Ultimately, as the high  $q$  asymptote is approached, the average rate of reaction exhibits a square-root dependence on  $k$ . This square-root dependence is characteristic of a first-order reaction in the thin-film limit as treated by penetration theory [cf. Danckwerts (1970)]. Figure 6 is particularly relevant to the discussion reviewed in FS addressing whether an observed dependence of the rate of reaction upon  $k$  establishes the absence of aqueous-phase diffusion limitation, showing that even though the rate of reaction is severely restricted by diffusion it continues to increase with increasing  $k$ . Consequently, the observation of an increase in reaction rate with increasing  $k$  cannot be taken as proof that a system under study is exhibiting the intrinsic, chemically limited rate.

The expressions given here lead to a criterion that may be used to test for diffusion limitation in experimental studies. From a measured average rate of uptake per unit volume of drop  $\bar{R}$ , one computes an apparent rate coefficient

$$k' \equiv \bar{R}/A_*, \quad (19)$$

and in turn the apparent diffusio-reactive parameter

$$q' = a(k'/D_a)^{1/2}. \quad (20)$$

If  $q' < 1.2$  then the average concentration  $A_{ss}$  closely

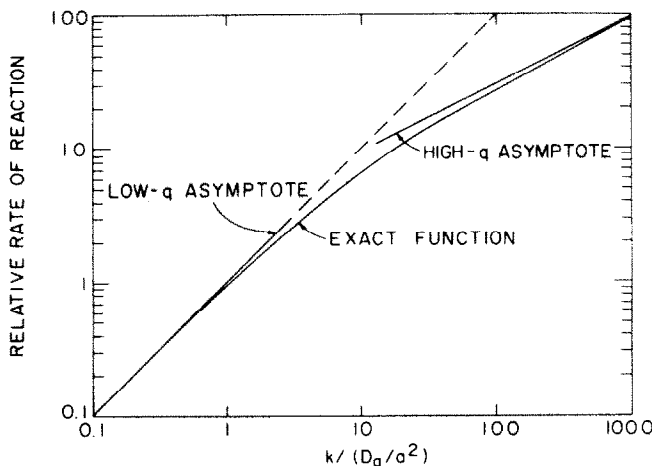


Fig. 6. Relative rate of reaction, at steady state, as a function of increasing first-order rate coefficient  $k$  for a fixed droplet radius  $a$  and diffusion coefficient  $D_a$ . Low- $q$  asymptote (unity-slope on log-log plot) gives rate in absence of diffusion-limitation. High- $q$  asymptote (slope = 1/2) shows continued increase in rate with increasing  $k$ , despite diffusion limitation.



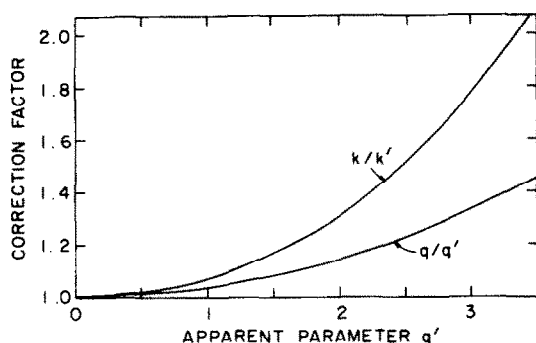


Fig. 7. Correction factors to determine true values of  $k$  and  $q$  from experimentally determined "apparent" values of  $q'$  and  $k'$  as a function of the apparent value  $q' = a(k'/D_g)^{1/2}$ . For  $q'$  beyond the range given see Equations (21a) and (22a).

approximates (within 10%) the surface concentration  $A_*$  and the estimate of  $k$  by Equation (19) is valid. If, however,  $q'$  is substantially greater than 1.2, then  $A_*$  significantly exceeds  $\bar{A}_{ss}$ , and there is significant diffusion limitation to the rate of uptake; i.e.  $k'$  evaluated by (19) underestimates the true value of  $k$ .

If it is found by evaluation of  $q'$  that diffusion limitation is significant, it is possible using the results given here to compute the true values of  $k$  and  $q$  from the apparent values  $k'$  and  $q'$ . To facilitate this we give in Fig. 7 the correction factors

$$k/k' = A_*/\bar{A}_{ss}, \quad (21)$$

and

$$q/q' = (A_*/\bar{A}_{ss})^{1/2}, \quad (22)$$

as a function of  $q'$ . For values of  $q'$  exceeding 3 these correction factors become [Equation (18b)]

$$k/k' \approx \left(\frac{q'}{3} + \frac{1}{q'}\right)^2, \quad q' \gtrsim 3, \quad (21a)$$

and

$$\frac{q}{q'} \approx \frac{q'}{3} + \frac{1}{q'}, \quad q' \gtrsim 3. \quad (22a)$$

As anticipated, the correction factors are quite close to unity for low values of  $q'$  but become quite appreciable for values of  $q'$  greater than 1. Thus, for example, the apparent rate coefficient  $k'$  computed from experimental data by Equation (19) will be lower by a factor of two than the actual value, for  $q'$  evaluated by Equation (20) equal to 3.4. It should be emphasized that these correction factors are exact only for reactions that are first-order in the concentration of the dissolved gaseous reagent. For reactions described by other rate laws the correction factor  $k/k'$  should be considered only an approximate index of the magnitude of the correction factor required.

#### Gas-phase diffusion and aqueous-phase reaction

We now address the question of diffusion limitation in the gas-phase. As in the case of the aqueous phase we consider mass transport in the gas phase to be

governed by molecular diffusion, appropriate in the absence of mechanically or convectively induced mixing. (If such mixing were applied, additional studies might be required to ascertain the characteristic time of that mixing.) The differential equation describing the gas-phase diffusion is

$$\frac{dG}{dt} = D_g \nabla^2 G, \quad r \geq a, \quad (23)$$

where  $G(r, t)$  is the concentration of gas-phase reagent, with boundary condition

$$G(\infty, t) = G_\infty. \quad (24)$$

We do not treat the time-dependent gas-phase problem since, as we have noted,  $D_g \gg D_a$ , and consequently the profile of  $\text{SO}_2$  concentration in the gas phase will rapidly adjust to accommodate changes in the aqueous-phase concentration profile. The question that we address therefore relates to the extent of departure of the steady-state or pseudo-state gas-phase concentration from a uniform profile equal to the bulk gas-phase concentration. We thus consider a pseudo-steady-state solution to Equation (23)  $G_{ss}(r)$  satisfying the condition of a prescribed amount of reagent entering the (spherical) droplet per unit time

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dG_{ss}}{dr} \right) = 0, \quad (25)$$

$$(4\pi a^2) D_g \left( \frac{dG_{ss}}{dr} \right)_{r=a} = \frac{4}{3} \pi a^3 \bar{R}; \quad (26)$$

here  $\bar{R}$  is the rate of material entering the droplet per unit volume of the droplet. The solution to Equation (25) with conditions (24) and (26) is

$$G_{ss}(r) = G_\infty - (\bar{R}a^3/3D_g)r^{-1}, \quad (27)$$

i.e. decreasing uniformly from the bulk value to the value at the surface of the drop

$$G_{ss}(a) = G_\infty - \bar{R}a^2/3D_g. \quad (28)$$

We are particularly interested in the fractional departure of  $G_{ss}(a)$  from the bulk value as a criterion for the lack of gas-phase diffusion limitation to the rate of uptake into the drop

$$1 - \frac{G_{ss}(a)}{G_\infty} = \bar{R}a^2/3D_g G_\infty \ll 1. \quad (29)$$

The criterion (29), which derives from a quantitative consideration of the decrease in the surface concentration of the reagent gas from its bulk concentration, may be seen to be equivalent to the intuitive criterion developed in Section 2 that  $\tau_{d,g} \ll \tau_{c,g}$ . It is this equivalence that led to the definition of  $\tau_{c,g}$  that was presented.

It is interesting to observe that there is a maximum rate  $R_{max}$  at which gas-phase reagent can be diffused into a droplet. This rate, which is attained when the surface concentration  $G(a) = 0$ , is given by

$$R_{max} \equiv 3 D_g G_\infty / a^2, \quad (30)$$

and serves as an index against which to compare a measured rate of uptake  $\bar{R}$  to test for gas-phase diffusion limitation. If  $\bar{R}/R_{\max}$  is appreciable, then the gas-phase concentration at the surface of the droplet  $G_{ss}(a)$  is appreciably less than that in the bulk  $G_{\infty}$ . Under the assumption of phase equilibrium at the surface of the droplet the same conclusion holds for the aqueous phase concentrations, namely that  $A_*$  is appreciably less than  $A_{\infty}$ , the surface concentration in phase equilibrium with the bulk gas-phase concentration. The correction factor here is

$$\begin{aligned} A_*/A_{\infty} &= G_{ss}(a)/G_{\infty} = 1 - \bar{R}/R_{\max} \\ &= 1 - \bar{R}a^2/3D_g G_{\infty}. \end{aligned} \quad (31)$$

This correction factor applies irrespective of the mechanism and order of the aqueous-phase reaction. We note also that in contrast to the case of aqueous-phase diffusion limiting, the rate of reaction can become entirely gas-phase diffusion controlled. In the limit as  $\bar{R}$  approaches  $R_{\max}$ , the rate of uptake becomes independent of  $k$  and depends on the first power of  $G_{\infty}$ , irrespective of reaction order. In this limit also  $\bar{R}$  exhibits a characteristic inverse square dependence on drop radius  $a$ .

Expression (31) may be simplified in the case of a first-order reaction in steady state, for which  $\bar{R}_{ss} = k\bar{A}_{ss}$ , to yield

$$A_{\infty}/A_* = 1 + (\bar{A}_{ss}/A_*)g, \quad (32)$$

where the factor  $(\bar{A}_{ss}/A_*)$  due to aqueous-phase diffusion limitation is given by Equation (18) and we introduce the dimensionless parameter

$$g \equiv kA_{\infty}/R_{\max}. \quad (33)$$

The parameter  $g$  is an index of gas-phase diffusion limitation:  $g \ll 1$  denotes the absence of gas-phase limitation whereas  $g \geq 1$  denotes potentially significant gas-phase diffusion limitation—definitely significant in the absence of aqueous phase diffusion limitation. From Equation (30) and noting also that  $A_{\infty} = \eta HRT G_{\infty}$ , we see that  $g$  is independent of gas- or aqueous-phase reagent concentration,

$$g = k\eta HRT a^2/3D_g.$$

Equation (32) may be combined with Equation (18) to obtain an expression for the overall (gas plus aqueous phase) magnitude of reduction of the rate of reaction due to diffusion limitation

$$\frac{A_{\infty}}{\bar{A}_{ss}} = \frac{1}{3 \left( \frac{\coth q}{q} - \frac{1}{q^2} \right)} + g, \quad (34)$$

where the two terms represent the contributions of aqueous and gas-phase diffusion limitation, respectively.

Equation (32) also permits us to formulate an overall criterion for the absence of diffusion limitation in either phase. In the absence of aqueous phase diffusion limitation ( $q \lesssim 1$ ),  $\bar{A}_{ss}/A_* = 1$ , and we obtain

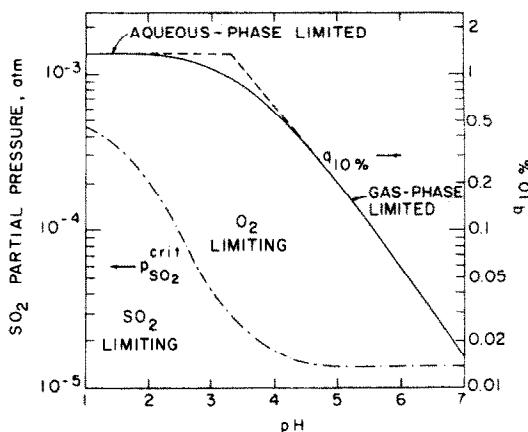


Fig. 8. Upper bound to  $q_s, q_{10\%}$ , such that diffusion limitation to the rate of reaction not exceed 10%. ---- represents individual gas-phase and aqueous-phase bounds; ——— represents bound from the combined effect. ···· gives the  $\text{SO}_2$  partial pressure  $p_{\text{SO}_2}^{\text{crit}}$  that demarcates regions in which  $\text{SO}_2$  or  $\text{O}_2$  diffusion limitation is more restrictive. Curves applicable to 25°C.

$$A_{\infty}/A_* = 1 + ka^2\eta HRT/3D_g = 1 + q^2\eta HRTD_a/3D_g.$$

Hence for  $A_*$  to exhibit departure from  $A_{\infty}$  by no more than 10% we obtain the upper bound upon  $q$

$$q \leq (0.3 D_g/\eta HRTD_a)^{1/2}. \quad (35)$$

This bound on  $q$  exhibits a pH dependence for  $\text{SO}_2$  because of the pH dependence of  $\eta$ . In Fig. 8 is shown as a function of pH the upper bound on  $q$  in order that the decrease in the rate of reaction not exceed 10% because of the limitation of either gas-phase or aqueous-phase diffusion. At low pH the aqueous-phase diffusion limitation is more restrictive, but above  $\text{pH} \approx 3.3$  the gas-phase diffusion limitation is more restrictive because of the strong increase in solubility with increasing pH.

In connection with this transition between aqueous- and gas-phase limitation to the rate of uptake of  $\text{SO}_2$  by water, it is interesting to observe that a transition at a similar pH is expected where the mechanism of mass transport is that of turbulent mixing. Liss (1971) [cf. also Brimblecombe and Spedding (1972)] has used empirical mass transport coefficients to conclude that under atmospheric conditions governing the uptake of  $\text{SO}_2$  by natural waters the uptake rate would be controlled entirely by gas-phase mass transport for pH greater than 2.8.

The recognition that there is a maximum rate  $R_{\max}$  at which material can be diffused to the surface of a drop motivates us to define one additional characteristic time

$$\tau_{\text{resg}} = A_{\infty}/R_{\max}. \quad (36)$$

This quantity is a measure of the time required to supply, by means of gas-phase diffusion, sufficient reagent to establish the equilibrium reagent concentration in aqueous droplets; i.e. the condition  $t \geq \tau_{\text{resg}}$  must be fulfilled before such an equilibrium

condition can be achieved. We note that  $\tau_{\text{reag}}$  may be related to  $\tau_{\text{d.g.}}$

$$\tau_{\text{reag}} = \frac{\eta HRT a^2}{3D_g} = \frac{\pi^2}{3} \eta HRT \tau_{\text{d.g.}} \quad (37)$$

and note also that because of the pH dependence of  $\eta$ ,  $\tau_{\text{reag}}$  may become quite appreciable at high pH. Thus for pH 6.5 [ $\eta HRT = 10^5 \text{ M(aq)/M(g)}$ ], and a droplet radius of 1 mm,  $\tau_{\text{reag}} \approx 1 \text{ h}$ . This point has been discussed also by Beilke and Gravenhorst (1978), who have presented curves showing the approach of the aqueous-phase S(IV) concentration to its equilibrium value as a function of time for various values of pH. (It should perhaps be pointed out that the leveling off of the uptake curves presented in Fig. 3 of Beilke and Gravenhorst is due simply to saturation of the drop by sulfur-IV and not to an increase in surface resistance as those authors stated.)

If the average steady-state aqueous-phase concentration departs significantly from  $A_\infty$ , then the time characteristic of reaching this steady-state reagent concentration will be less than  $\tau_{\text{reag}}$ , being given rather by

$$\tau'_{\text{reag}} = \bar{A}_{ss}/R_{\text{max}}, \quad (38)$$

where  $\bar{A}_{ss}$  is given by Equation (34).

One final point that should be emphasized is that the discussion of gas-phase mass transport, as also for aqueous phase, has assumed that the only mixing process occurring is that of molecular diffusion. The distance scale ("half-distance") characterizing the fall-off in gas-phase concentration is equal to the droplet radius  $a$ . For larger droplets ( $a > 1 \text{ mm}$ ) mixing on this distance scale is highly susceptible to convection or to mechanically induced gas motion. Consequently the correction factor [Equation (31)] should be initially considered an index of the magnitude of the potential error arising from gas-phase diffusion limitation and should be applied only when one is confident that diffusion is the dominant gas-phase mixing process. Similarly, while the magnitude of  $\tau_{\text{reag}}$  given by Equation (37) may substantially overestimate the time required to supply the reagent to the droplet, this quantity should nonetheless serve as a guide for concern in the design and interpretation of experiments.

#### Phase equilibrium and aqueous-phase reaction

We examine here the conditions under which the rate of uptake by an aqueous medium may be restricted by the finite rate at which phase equilibrium is achieved at the gas-liquid interface. This equilibrium is brought about by the rate of collisions of gas-phase molecules with the surface (Danckwerts, 1970), which is given by

$$\sigma_+ = \frac{1}{4} G(a) \bar{v} \xi, \quad (39)$$

where  $\sigma$  is the rate per unit surface area, moles  $\text{cm}^{-2} \text{ s}^{-1}$ , and the other symbols have been defined

above. Expressing  $G(a)$  in terms of the hypothetical aqueous phase concentration  $A_*$  in equilibrium with  $G(a)$ ,  $A_* \equiv \eta HRT G(a)$ , we obtain

$$\sigma_+ = \bar{v} A_* \xi / 4\eta HRT.$$

The rate of material leaving the aqueous phase back into the gas phase is based upon the actual aqueous phase surface concentration  $A(a)$  and is

$$\sigma_- = \bar{v} A(a) \xi / 4\eta HRT,$$

whence the net rate is

$$\sigma = \sigma_+ - \sigma_- = \frac{\bar{v}}{4\eta HRT} [A_* - A(a)]. \quad (40)$$

This net rate replaces Equation (13) as the boundary condition for the differential equation describing the steady-state concentration profile, Equation (12); i.e.

$$-D_a \left( \frac{\partial A}{\partial r} \right)_{r=a} = \sigma = \frac{\bar{v} \xi}{4\eta HRT} [A_* - A(a)]. \quad (41)$$

The solution to Equation (12) with boundary condition (41) is the same as Equation (14) except that  $A_*$  is replaced by  $A(a)$ ; the ratio of  $A_*$ , the equilibrium surface concentration, to  $A(a)$ , the actual surface concentration, is

$$A_*/A(a) = 1 + \left( \frac{\tau_{\text{phase}}}{\tau_{\text{c.a.}}} \right)^{1/2} \frac{q}{3} \left[ 3 \left( \frac{\coth q}{q} - \frac{1}{q^2} \right) \right], \quad (42)$$

where we have made use of the definitions (1a), (5) and (15). The factor in brackets is equal to  $\bar{A}_{ss}/A_*$ , Equation (18). For low values of  $q$ , i.e. corresponding to the absence of aqueous-phase diffusion limitation

$$A_*/A(a) = 1 + \left( \frac{\tau_{\text{phase}}}{\tau_{\text{c.a.}}} \right)^{1/2} \frac{q}{3}, \quad q < 1, \quad (42a)$$

whereas for high values of  $q$

$$A_*/A(a) = 1 + (\tau_{\text{phase}}/\tau_{\text{c.a.}})^{1/2}, \quad q \geq 10. \quad (42b)$$

Equation (42) expresses the decrease in surface concentration  $A(a)$  resulting from depletion of the aqueous phase reagent by reaction faster than the phase equilibrium can be restored. For  $\tau_{\text{c.a.}} \gg \tau_{\text{phase}}$ , this depletion is negligible, as anticipated, and thus the surface concentration  $A(a)$  is equal to the concentration in equilibrium with the gas phase concentration at the surface  $G_{ss}(a)$ . However, for  $\tau_{\text{phase}}$  of the order of or exceeding  $\tau_{\text{c.a.}}$  there may be an appreciable decrease in  $A(a)$  relative to  $A_*$ .

Equation (42a) permits evaluation of a bound on  $q$  in order that  $A(a)$  not depart from  $A_*$  by more than 10%, viz.

$$q \leq (0.3 \bar{v} \xi / 4\eta HRT D_a)^{1/2}. \quad (43)$$

Comparison of Equation (43) with Equation (35) (the bound on  $q$  that gas-phase diffusion limitation not exceed 10%) shows that the phase equilibrium constraint is less restrictive than the gas-phase constraint for  $a > 4 D_g / \bar{v} \xi$ , but is more restrictive for droplets of

smaller radius. Assuming that the sticking coefficient  $\xi = 1$ , then the constraint [Equation (43)] is more restrictive than Equation (35) only for a  $< 0.16 \mu\text{m}$ .

#### Mass transport of $\text{O}_2$

For the aqueous-phase oxidation of sulfur-IV by dissolved oxygen we must address also mass transport limitation for reagent  $\text{O}_2$ . Assuming the reaction to be first order in  $[\text{O}_{2(\text{aq})}]$  we may proceed entirely analogously to our treatment for  $\text{SO}_2$ . This treatment yields the bound  $q_{\text{O}} \leq 1$  from aqueous-phase diffusion as well as the bounds [Equations (35) and (43)] from gas-phase and surface considerations. Evaluation of the latter two bounds for  $\text{O}_2$  establishes them to be far less restrictive than the aqueous-phase diffusion constraint, so we may restrict our consideration to aqueous-phase mass transport only.

By analogy to  $\text{SO}_2$ , the parameter  $q_{\text{O}}$  is equal to  $a(k_{\text{O}}/D_{\text{O}_2(\text{aq})})^{1/2}$ , where

$$k_{\text{O}} = - (d[\text{O}_{2(\text{aq})}]/dt) / [\text{O}_{2(\text{aq})}].$$

By stoichiometry

$$d[\text{O}_{2(\text{aq})}]/dt = \frac{1}{2} d[\text{S(IV)}]/dt,$$

and hence  $q_{\text{O}}$  is related to  $q$  for S(IV), which we now denote as  $q_{\text{S}}$ , by

$$q_{\text{O}} = q_{\text{S}} (D_{\text{S(a)}} \eta H_{\text{SO}_2} p_{\text{SO}_2} / 2 D_{\text{O}_2(\text{a})} H_{\text{O}_2} p_{\text{O}_2})^{1/2}. \quad (44)$$

For diffusion limitation to be negligible ( $< 10\%$ )  $q_{\text{O}} \leq 1.3$ . Hence Equation (44) may be considered to place a further bound on  $q_{\text{S}}$ , viz.

$$q_{\text{S}} \leq 1 q_{\text{S,O}}. \quad (45)$$

where

$$q_{\text{S,O}} \equiv 1.3 (2 D_{\text{O}_2(\text{a})} H_{\text{O}_2} p_{\text{O}_2} / D_{\text{S(a)}} \eta H_{\text{SO}_2} p_{\text{SO}_2})^{1/2}. \quad (46)$$

If  $q_{\text{S,O}}$  is lower than the bound  $q_{10\%}$  from aqueous or gas phase diffusion, then the constraint [Equation (45)] will be a more restrictive limitation on  $q_{\text{S}}$ . From Equation (46) it is seen that this condition will obtain for values of  $\text{SO}_2$  partial pressure exceeding a critical value defined as

$$p_{\text{SO}_2}^{\text{crit}} \equiv \frac{3.5 D_{\text{O}_2(\text{a})} H_{\text{O}_2} p_{\text{O}_2}}{D_{\text{S(a)}} \eta H_{\text{SO}_2} q_{10\%}^2}. \quad (47)$$

This critical value of  $p_{\text{SO}_2}$  was evaluated as a function of pH for  $p_{\text{O}_2} = 0.2 \text{ atm}$  and  $25^\circ\text{C}$  and is given in Fig. 8. [Here we have made use of values of  $H_{\text{O}_2} = 1.27 \times 10^{-3} \text{ M atm}^{-1}$  (Loomis, 1928) and of  $D_{\text{O}_2(\text{a})} = 2.3 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  (Himmelblau, 1964).] It is seen that mass-transport limitation to the rate of reaction by  $\text{O}_2$  in the absence of  $\text{SO}_2$  limitation is significant only at rather high  $\text{SO}_2$  partial pressures. Of course, mass transport limitation by both  $\text{SO}_2$  and  $\text{O}_2$  might occur and should be examined if necessary.

Table 2. Summary of uniformity conditions, characteristic times and criteria

Uniformity conditions		
Aqueous phase:	$A(r, t) = A(a)$	
Surface:	$A(a) = A_* [\equiv \eta HRTG(a)]$	
Gas phase:	$G(r, t) = G_\infty$	
Overall:	$A(r, t) = \eta HRTG_\infty$	
Characteristic times		
Phase equilibrium	$\tau_{\text{phase}}$	$D_a (4\eta HRT/v\xi)^2$
Hydrolysis and 1st ionization	$\tau_{a1}$	$\{k_{a1} + k_{-a1}([\text{H}^+] + [\text{HSO}_3^-])\}^{-1}$
2nd ionization	$\tau_{a2}$	$\{k_{a2} + k_{-a2}([\text{H}^+] + [\text{SO}_3^{2-}])\}^{-1}$
Aqueous chemical	$\tau_{\text{c.a.}}$	$A/R (= A_*/\bar{R}) \dagger (= k^{-1}) \ddagger$
Aqueous diffusion	$\tau_{\text{d.a.}}$	$a^2/\pi^2 D_a$
Gaseous chemical	$\tau_{\text{c.g.}}$	$G_\infty/\bar{R}$
Gaseous diffusion	$\tau_{\text{d.g.}}$	$a^2/\pi^2 D_g$
Reagent supply	$\tau_{\text{reag}}$	$\bar{A}_\infty/R_{\text{max}} = \frac{\pi^2}{3} \eta HRT \tau_{\text{d.g.}}$
Intrinsic rate criteria		
$\tau_{a1}, \tau_{a2}, \tau_{\text{phase}} \ll \tau_{\text{c.a.}}$ — intrinsic rate is rate of S(IV) oxidation		
Steady-state criteria		
SS1. $t \gg \min(\tau_{\text{c.a.}}, \tau_{\text{d.a.}})$	— pseudo steady state in aqueous phase for fixed $G(a)$	
SS2. $t \gg \tau_{\text{d.g.}}$	— pseudo steady state in gas phase for fixed surface sink rate	
SS3. $t \gg \tau_{\text{reag}}$	— overall steady state provided SS1 and SS2 are fulfilled	
Steady-state spatial uniformity criteria		
$\tau_{\text{d.a.}} \ll \tau_{\text{c.a.}}$ — aqueous phase		
$\tau_{\text{d.g.}} \ll \tau_{\text{c.g.}}$ — gas phase		

† Valid under condition of aqueous-phase uniformity.

‡ For first-order reaction.

## 4. SUMMARY AND CONCLUSIONS

The aqueous-phase oxidation of  $\text{SO}_2$ , as any gas-liquid reaction, inevitably involves competition between mass transport and reaction. To facilitate understanding of this competition we have identified characteristic times associated with the several steps in the overall process and have presented expressions whereby these characteristic times may be evaluated for reactions in spherical drops. Examination of these characteristic times permits the time for the reaction system to reach steady state in a particular situation to be readily ascertained. Similarly, by comparison of these characteristic times it may be ascertained whether a measured rate of reaction is equal to the intrinsic reaction rate or is limited by mass transport in the gas-phase, at the air-water interface, or in the aqueous phase. Table 2 presents this comparison and indicates the criteria that must be fulfilled for spatial and temporal uniformity to be achieved under experimental conditions or in the ambient atmosphere. The three steady-state criteria must be satisfied in order for steady-state to be attained. After the steady state is reached, the concentration profiles may or may not be uniform, and phase equilibrium may or may not be established at the surface, depending upon the relative magnitudes of the several characteristic times. The resulting concentration profiles in the two phases and at the interface are illustrated schematically in Fig. 9.

A theoretical model was presented whereby the extent of decrease in reaction rate may be calculated for each of the three mass-transport limiting processes, for a reaction that is first-order in the concentration of the dissolved reagent species, and for mass transport in

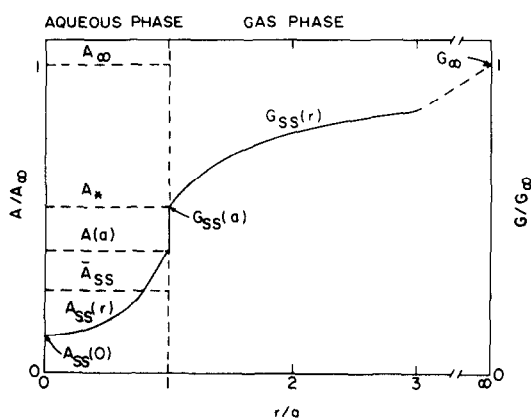


Fig. 9. Schematic representation of steady-state concentration profiles in gas ( $G$ ) and aqueous ( $A$ ) phases; gas-phase concentrations are scaled relative to aqueous phase concentrations by the factor  $\eta HRT$ .  $G_\infty$  represents bulk gas-phase concentration;  $A_\infty$  represents aqueous phase concentration in equilibrium with  $G_\infty$ .  $G_{ss}(r)$  reflects decrease in  $G$  due to gas-phase diffusion limitation.  $A_*$  is aqueous phase concentration in equilibrium with  $G_{ss}(a)$ . The difference between  $A_*$  and  $A(a)$  represents departure from phase equilibrium.  $A_{ss}(r)$  reflects decrease in  $A$  due to aqueous phase diffusion limitation.  $A_{ss}(0)$  and  $\bar{A}_{ss}$  represent steady-state concentrations at the center of the drop and averaged over the drop, respectively.

each of the two phases occurring by molecular diffusion. This treatment led to correction factors that may be used for such reaction systems to infer the intrinsic rate constant from laboratory measurements conducted under mass-transport limiting conditions. In principle this treatment might be extended either analytically or numerically to other reaction or mass-transport mechanisms. However, in practice it may be difficult to establish these mechanisms for the reaction system under investigation, thus precluding the precise evaluation of the magnitude of systematic error resulting from mass-transport limitation. Consequently, experiments to determine the kinetics of reactions in aqueous droplets should be conducted under conditions in which mass-transport limitation to the overall rate is minimized.

This theoretical framework has been applied (Freiberg and Schwartz, 1980) to an examination of laboratory studies of  $\text{SO}_2$  oxidation in suspended droplets and to consideration of mass transport limitation to the rate of oxidation of  $\text{SO}_2$  in clouds and fogs.

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## APPENDIX

## TIME-DEPENDENT SOLUTION

The purpose of this appendix is to provide insight into the time dependence of the aqueous phase reagent concentration following sudden exposure of a droplet to a gas-phase reagent, and to establish the limit of validity of the steady-state treatment employed in the text.

The partial differential equation describing the time and space evaluation of the concentration  $A$  of an aqueous-phase reagent undergoing first-order kinetics ( $\partial A/\partial t = -kA$ ) in a spherically symmetric geometry is given as a function of radius  $r$  and time  $t$  as

$$\frac{dA}{dt} = D_a \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial A}{\partial r} \right) - kA. \quad (\text{A1})$$

The boundary conditions to Equation (A1) for a droplet initially free of dissolved reagent that is suddenly (at time

$t = 0$ ) exposed to a gas-phase reagent that induces a constant concentration  $A_a$  at the surface ( $r = a$ ) are

$$A(r, 0) = 0, \quad r < a, \quad (\text{10a})$$

$$A(a, t) = A_a, \quad t > 0. \quad (\text{10b})$$

Equation (A1) with conditions (10) may be solved in a variety of ways—separation of variables and series solution, Laplace transform, or the method of Danckwerts (1951) utilizing the solution of Carslaw and Jaeger (1959) for the corresponding problem without reaction—to yield the solution

$$\frac{A(r, t)}{A_a} = \frac{1 \sinh qz}{z \sinh q} + \frac{21}{\pi z} \times e^{-y} \sum_{n=1}^{\infty} (-1)^n n \frac{\sin(n\pi z) \exp[-y(n\pi/q)^2]}{(q/\pi)^2 + n^2}, \quad (\text{A2})$$

where, for compactness, we have introduced  $y = kt$  and  $z = r/a$ . (The first term in (A2) is of course the steady-state solution, Equation 14.) In Fig. A1 are plotted concentration profiles  $A(r, t)$  for several values of  $t$ , for the diffusio-reactive parameter  $q = 1.5$ . At early times, as expected, the penetration of reactant into the drop is quite small, but this penetration rapidly approaches the steady-state profile. Figure A1 may be compared with the situation for diffusion in the absence of reaction, corresponding to  $q = 0$ , that has been treated by Crank (1975) [cf. also Carslaw and Jaeger (1959)]. In the absence of reaction the concentration profile becomes uniform at large time, whereas for first-order reaction treated here the concentration function approaches a non-uniform steady-state profile such as has been given in Fig. 4.

In order to consider the time dependence of the rate of reaction averaged over the drop,  $\bar{R} = k\bar{A}$ , we have computed (cf. Equation 17) the time-dependent average concentration

$$\frac{\bar{A}(t)}{A_a} = 3 \left( \frac{\coth q}{q} - \frac{1}{q^2} \right) - \frac{6}{\pi^2} e^{-y} \sum_{n=1}^{\infty} \frac{\exp[-y(n\pi/q)^2]}{(q/\pi)^2 + n^2}. \quad (\text{A3})$$

Examples of this time dependence of  $\bar{A}$  are given in Fig. A2 for several values of  $q$ . It may be seen that for low values of  $q$  the approach to steady state is quite rapid compared to the characteristic time of the reaction,  $k^{-1}$ , but that significant departure from the steady-state average persists for greater time as  $q$  increases. It is readily established from Equation (A3) that the departure of  $\bar{A}$  from its steady-state value is bounded by a simple product of exponentials involving the rates of diffusion and reaction,

$$\frac{\bar{A}_{ss} - \bar{A}(t)}{\bar{A}_{ss}} \leq e^{-y} e^{-y(n\pi/q)^2} \equiv e^{-kt} e^{-(D_a \pi^2/a^2)t}. \quad (\text{A4})$$

From this result it is seen that the approach of  $\bar{A}$  to its steady state value at large  $q$  is governed by the characteristic time of reaction, not by the much greater characteristic time of diffusion.

We wish to consider now the amount or mass of material  $M(t)$  taken up by the drop as a function of time subsequent to the commencement of the exposure. This amount of uptake,  $M(t)$ , includes the sum of reactant and product mass taken up by exposure for a period  $t$ , and thus represents an experimentally measurable quantity, i.e. the quantity that would be determined by chemical analysis conducted subsequently.

The expression for  $M(t)$  is conveniently obtained by first computing the flux of reactant into the drop,  $F(t)$ , which is governed by the rate of aqueous-phase diffusion at the surface

$$F(t) = 4\pi a^2 D_a \left( \frac{\partial A(r, t)}{\partial r} \right)_{r=a}. \quad (\text{A5})$$

The amount of material in the drop is then given as

$$M(t) = \int_0^t F(t') dt'. \quad (\text{A6})$$

The flux characterizing the present problem may be obtained from Equation (A2) by Equation (A5), and has been given by

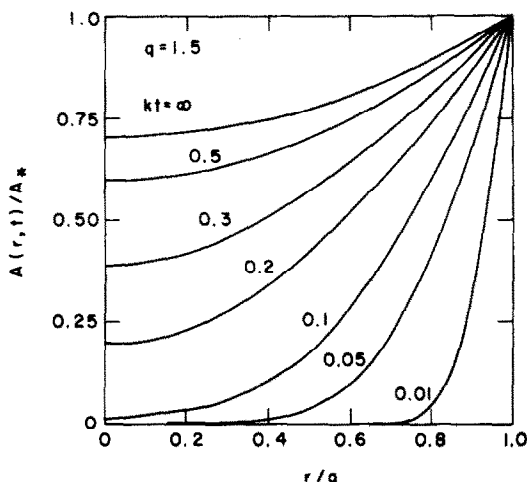


Fig. A1. Values of the time- and space-dependent reagent concentration  $A(r, t)$  as a function of  $r$  for indicated values of  $kt$ , and for the diffusio-reactive parameter  $q = a(k/D_a)^{1/2} = 1.5$ . With increasing time the radial concentration function approaches the non-uniform steady-state profile; contrast Fig. 6.1 of Crank (1975) displaying profiles for diffusion in the absence of reaction, i.e.  $q = 0$  in the present notation.

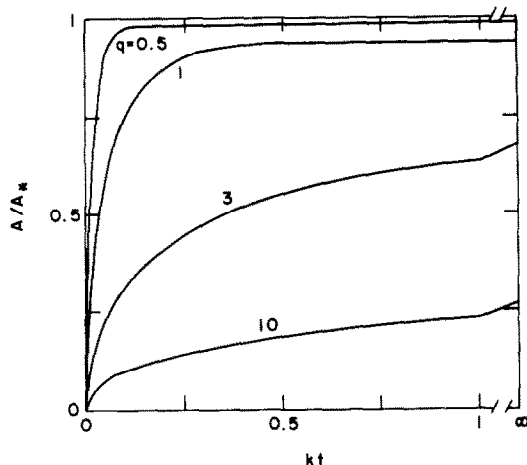


Fig. A2. Reagent concentration  $\bar{A}$  averaged over droplet volume, ratioed to concentration at the surface  $A_*$ , as a function of time, for indicated values of  $q$ . Infinite time or steady state values are indicated on right hand axis.

Dankwerts (1951) [cf. also Crank (1975)] as

$$F(t) = (4\pi a^3/3)kA_* \times \left[ 3 \left( \frac{\coth q}{q} - \frac{1}{q^2} \right) + \frac{6}{q^2} e^{-y} \sum_{n=1}^{\infty} \frac{n^2 \exp[-y(n\pi/q)^2]}{n^2 + (q/\pi)^2} \right] \quad (\text{A7})$$

The first term in Equation (19) is seen to equal the steady state rate of reaction,  $\bar{R}_{ss} = k\bar{A}_{ss}$ , multiplied by the volume of the drop

$$F_{ss} = (4\pi a^3/3)kA_* \left[ 3 \left( \frac{\coth q}{q} - \frac{1}{q^2} \right) \right] \quad (\text{A8})$$

The second term in Equation (A7) is initially large as material rapidly diffuses into the drop to establish  $\bar{A}_{ss}$ , but ultimately decays. This time dependence of the flux is shown in Fig. A3 for several values of  $q$ .

As with the average concentration we are concerned with the departure of the flux from its steady-state value and with

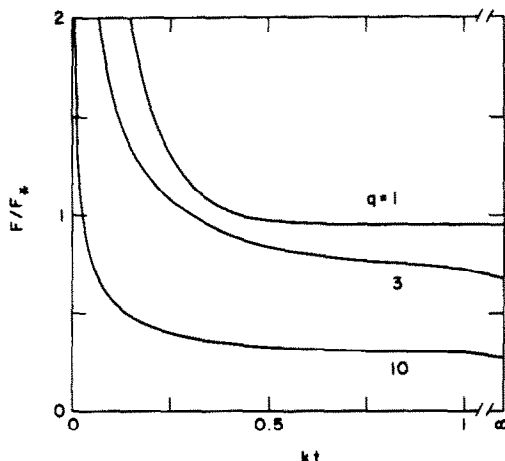


Fig. A3. Flux of reagent entering drop as a function of time for indicated values of  $q$ . Flux is normalized to the steady-state flux for reagent concentration in equilibrium with the gas-phase concentration,  $F_* = (4\pi a^3/3)kA_*$ .

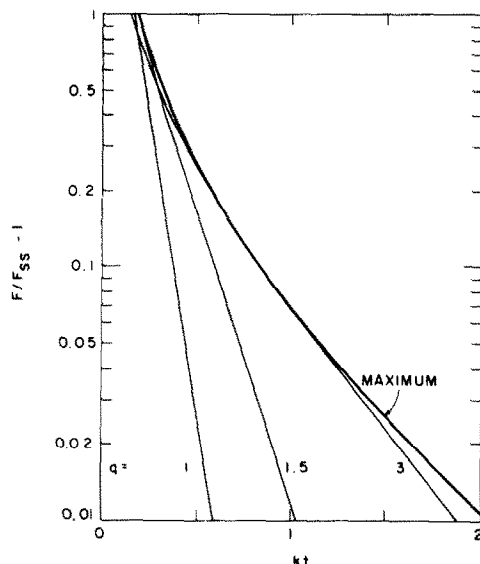


Fig. A4. Time dependence of the relative difference between the flux into the drop at time  $t$  and the steady state flux into the drop, for indicated values of  $q$ . Dark curve at right of figure represents the envelope of the several curves and constitutes an upper bound on this relative difference for all values of  $q$ .

the time dependence of the relaxation to the steady-state value. In Fig. A4 this relative departure,  $[F(t)/F_{ss}]^{-1}$ , is plotted as a function of time for several values of  $q$ . The several curves decrease sharply on the time scale of reaction, and in fact the entire set is bounded by a sharply decreasing envelope. This envelope serves to set an upper limit to the time required for the flux into the drop to reach its steady-state value. For example, at  $t = k^{-1}$  the flux will not exceed the steady-state flux by more than 6.8%, and at  $t = 2k^{-1}$  by more than 1.1%. Since this flux is equivalent [by Equations (A5) and (A6)] to the experimentally determined "rate of reaction" (in fact, rate of uptake), it is thus established that the steady state expressions may be employed at times greater than, say,  $(1 \text{ or } 2)k^{-1}$ , depending on the desired accuracy.

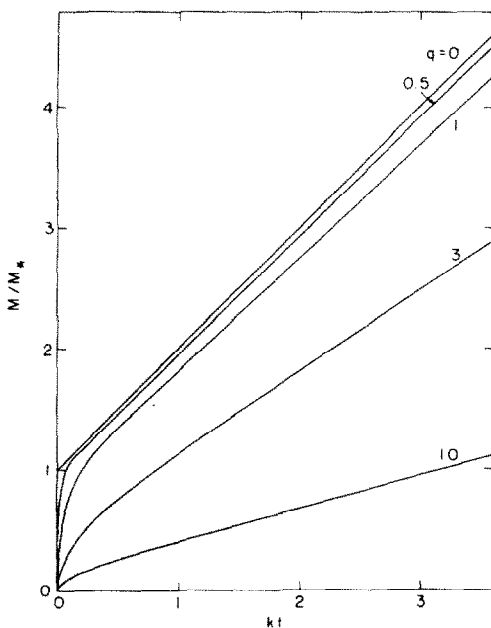


Fig. A5. Amount of material  $M(t)$  (sum of reagent plus product) taken up by droplet as a function of time, for indicated values of  $q$ . Amount of material is normalized to the amount of reagent present in the drop in equilibrium with the gas-phase concentration,  $M_* = (4\pi a^3/3)A_*$ .

Equation (A7) can be integrated over time (Equation A6) to give the amount of material in the drop

$$M(t) = (4\pi a^3/3)A_* \left\{ \frac{3}{2} \left( \frac{\coth q}{q} - \operatorname{csch}^2 q \right) - \frac{6}{\pi^2} e^{-y} \sum_{n=1}^{\infty} \frac{n^2 \exp[-y(n\pi/q)^2]}{[n^2 + (q/\pi)^2]^2} + 3 \left( \frac{\coth q}{q} - \frac{1}{q^2} \right) y \right\}. \quad (\text{A9})$$

An equivalent expression, except for an apparent typographical error, has been given by Crank (1975). Equation (A9) gives the functional form corresponding to a set of experimental measurements of uptake by a drop initially free of solute that is exposed to the reactive gas for a period of time  $t$ . This amount of uptake is shown in Fig. A5 for several values of  $q$ . For  $q=0$ , corresponding to infinitely fast diffusion, the amount of material taken up rises instantaneously to  $M_* = (4\pi a^3/3)A_*$ , the amount of reactant that would be in the drop in equilibrium with the gas-phase concentration, and then increases linearly with time as reaction proceeds permitting further uptake of reagent. For small but finite values of  $q$ ,  $\leq 0.5$ , the uptake curves closely approach the  $q=0$  function, but for greater values of  $q$ , there is a significant lag in achieving the steady state rate, as well as the departure of this rate from the ideal rate (slope of one on this plot) that has already been discussed. As noted in the above discussion the departure from the steady state rate decays with the time constant of the reaction, permitting the use of steady-state expressions developed above for times greater than  $(1 \text{ or } 2)k^{-1}$ .