Gas Absorption into a Moving Spheroidal Water Drop

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ABSTRACT

Theoretical and experimental studies have been carried out to describe the absorption of sulfur dioxide by moving spheroidal water drops under transient flow conditions. These investigations allow the determination of the rate at which SO$_2$ is scavenged from air by deformed spheroidal freely falling water drops. First, the theoretical models in the case of spheroidal water drops will be presented. For drops smaller than 1 mm in diameter, modeling is based on numerical solutions of Navier–Stokes and convective-diffusion equations, which describe transient flow and concentration fields, respectively, both in liquid and gas phases. For drops larger than 1 mm in diameter, modeling is based on scaling of interfacial agitation taking into account the effect of turbulent mixing and oscillation inside the drops. Second, an experimental device involving a 5-m rain shaft is presented in order to study SO$_2$ absorption and to verify the theoretical models for spheroidal water drops. The predicted sulfur concentrations inside the drop are compared with the experimental results for three categories of experiments (reversible absorption, irreversible absorption, and desorption). Adequate correlation between theory and experiment was obtained for a specified value of the aspect ratio $E$, which is a function of the equivalent diameter of the drop.

1. Introduction

Removal of gases from polluted air and gas streams by water drops has been identified as an important mass transfer process for air pollution control, industrial processes, technological research, and many engineering disciplines. The most interesting problem is the scavenging of sulfur dioxide by clouds and rain drops as it is responsible for acid deposition, influences precipitation and chemical composition, contributes to aquatic deterioration and building materials, possibly reduces agricultural productivity, and can damage human health. A knowledge of mass transfer to drops is of fundamental interest to many scientific and research fields involving spray and atmospheric systems as well as wet deposition. A large number of mathematical models and experimental investigations have been devoted to this problem.

For drops falling in a gas of high solubility (in this case resistance to penetration occurs in the external gas phase) a survey of the literature (Kaji et al. 1985; Altwickier and Lindhjem 1988) shows that there are a number of good theoretical models and experimental correlations for the prediction of gas film–mass transfer coefficients around a fluid. Recent studies, however, have shown that numerous models for the prediction of mass transfer coefficients into drops are not sufficiently trustworthy. This is particularly true for the absorption of low solubility gases (in this case resistance to penetration occurs in both the liquid and the gas phases). Therefore, a better knowledge of the mass transfer mechanism for absorption of gases by water drops is needed and is essential for the prediction and modeling of liquid mass transfer coefficients. It is of interest to remind the reader of the main models.

Newman (1931) was probably the first to propose an analytical solution to the concentration fields inside small stagnant drops, which are almost perfectly spherical in shape. However, it is well known that for most liquid systems, drops are not stagnant, and that an internal convective circulation exists that significantly affects the mass transfer rate to the drop. Kronig and Brink (1950), Johnson et al. (1967), Hidy (1970), and Watada et al. (1970) used flow fields described by the Hadamard and Rybczinski analytical solutions to solve the convective-diffusion equation under steady-state flow conditions. Unfortunately, these flow fields are only valid when the Reynolds number, derived from the terminal velocity and the drop diameter, is less than unity. For intermediate Reynolds numbers, Johnson et al. (1967) and Watada et al. (1970) solved the convective-diffusion equation to describe gas absorption by liquid drops using flow fields described by approximate solutions to the Navier–Stokes equations (Hamielec et al. 1967; Rimon and Cheng 1969; Leclair et
Several recent studies have been devoted to the description of sulfur dioxide absorption into spherical water drops using the numerical solutions of the Navier–Stokes equations. Baboolal et al. (1981) were the first to use the flow fields reported by Leclair et al. (1972). Recently, Amokrane et al. (1993) developed a full model of liquid sphere drop gas mass transfer coupled to the flow fields of Caussade and Saboni (1992) who solved numerically the Navier–Stokes equations inside and outside a freely falling spherical water drop. In general, drops remain spherical at moderate Reynolds numbers (drops less than 1 mm in diameter) if surface tension forces are sufficiently strong. But, a drop moving freely in a viscous fluid tends to deform from a spherical to a spheroidal shape for diameters greater than 1 mm, and generally the deformation is accompanied by an oscillation of the shape of the drop, in relation to wake shedding, which also significantly affects the mass transfer rate.

For drops larger than 1 mm in diameter a great number of parameterized models have been developed that characterize interfacial agitation processes inside drops due to turbulence mixing and oscillation. Some experimental measurements are inconsistent with others, and some models disagree widely from measurements. Some observations concerning the rigid circulating and oscillating behavior of drops were made by Calderbank and Korchinski (1956). The conclusion was reached, on both experimental and theoretical grounds, that circulation within a liquid drop results in an effective mass diffusivity of 2.25 times the molecular value. The same results have also been attained by Walcek et al. (1984) on the SO$_2$ mass transfer rate within drops larger than 1.1 mm in diameter. They have introduced an effective liquid phase diffusivity of 18 times the molecular one to explain the mass transfer rate. Handlos and Baron (1957) developed a theoretical model for liquid sphere drops with the assumptions that the transfer process is due to internal turbulent movement of the drop and that the internal flow field is expressed by Hadamard’s equation. In that case, theory and experimental data conflict. Angelo et al. (1966) proposed to relate the internal mass transfer coefficient to the oscillation frequency of the drop. The usual form of oscillation is the prolate–oblate type about an equilibrium spheroidal shape. Ruckenstein (1967) postulated that the concentration of the drop is homogeneous and the transfer process occurs in a very thin boundary layer adjacent to the interface. The expression of the internal mass transfer coefficient is deduced using the linearization of Hill’s vortex solution near the liquid surface. Ramachandran (1985) postulated a model in which the internal flow field was expressed by Hill’s vortex with weak velocities less than 7.5 times Hill’s velocities.

However, a number of experimental studies of gas absorption into water drops have been reported in the literature. Thus, Garner and Lane (1959) used a wind tunnel to study CO$_2$ absorption by two large drop sizes (4.22 and 5.85 mm) suspended in a gas stream. Low correlation is shown between experimental results and the values predicted previously by Kronig and Brink (1950). Beilke and Georgii (1968) used water drops to determine the rate of SO$_2$, NO$_2$, and CO$_2$ scavenging the air. After the water sprays had passed through the gas chamber, they were collected and recirculated through the chamber again until the gas was washed out. In this case, the rate at which SO$_2$ is scavenged by recirculated drops is different from the rate determined using continually reforming drops. Barrie and Georgii (1976) studied the absorption of SO$_2$ by only 2-mm large drops, which were suspended from a fixed support at the plastic tip of a glass capillary tube, rather than being allowed to fall freely at terminal velocity through the air. Under such conditions, drops may lose their shape and the resulting deformation considerably affects the SO$_2$ absorption by drops. Walcek et al. (1981) used a 33-m long shaft in which drops were allowed to reach their terminal velocity before they passed, for a specified time, through a column of variable length filled with a known concentration of SO$_2$. A good correlation between the experimental data and the values predicted from the theoretical model of Baboolal et al. (1981) was found for sphere drops with a radius less than 500 μm. For drops larger than 1.1 mm in diameter an effective diffusivity was introduced in the Kronig and Brink model to obtain correlation between predicted and observed concentrations. Kaji et al. (1985) studied the SO$_2$ absorption of water drops with a constant diameter of 2.2 mm. The drops were formed approximately every 2 s and then accelerated through an absorption column (41-mm inner diameter) with a variable length of 23–113 cm, which was filled with a mixture of SO$_2$ and N$_2$ with SO$_2$ concentrations of 620, 1126, and 1968 ppm. The authors only determined the liquid film mass transfer coefficient, which remained relatively constant through the fall, decreasing only from 0.035 to 0.0275 cm$^2$s$^{-1}$. Altwicker and Lindhjem (1988) determined liquid-side mass transfer coefficients of drops soon after formation, <0.1 s, for specific ranges. The method of drop production resembled that of sprays, and monosized drops were investigated. Approximate constant mass transfer coefficients were found for this system. However, the droplet velocities can be considerably higher than terminal velocities.

In order to improve the previous theoretical models, eliminate some of the deficiencies of earlier experiments, and help clarify the absorption behavior of sulfur dioxide into water drops for various absorption times and deformation characteristics, we have developed a theoretical and experimental study of the SO$_2$ scavenging rate into freely falling spheroidal water drops. In the first part, we describe two approaches. For drops smaller than 1 mm in diameter, the SO$_2$ absorption may be obtained from numerical solutions to the convective-diffusion equation coupled to numerically derived flow...
fields inside and outside drops of arbitrary aspect ratios. For drops larger than 1 mm in diameter, we propose a model based on the interfacial liquid friction velocity as the velocity scale and the drop diameter as the length scale to characterize the agitation process and the internal convective circulation. In our approach, we consider nonoscillating deformed circulating drops with a fixed shape represented by an oblate spheroid, which seems to be a good compromise between a stagnant drop and an oscillating drop. The theoretical predictions thus obtained are verified by means of a 5-m rain shaft described in the second part of this paper.

2. The numerical model for small drops

The present model involving the complete, time-dependent, convective-diffusion equation inside and outside liquid water drops with diameters less than 1 mm falling under the influence of gravity through the air can be expressed as

$$\frac{\partial c}{\partial t} + \mathbf{u} \cdot \nabla c = D_a \nabla^2 c + R_s, \quad (1)$$

where \(c\) is the sulfur local dimensional concentration at a given time \(t\) inside or outside the drop, \(\mathbf{u}\) is the prevailing velocity field covering the area or volume over which the equation is being applied. \(D_a\) is the Fickian diffusion coefficient assumed to be independent of the concentration, and \(R_s\) is the chemical source term.

Numerical solutions of Eq. (1) require knowledge of the flow fields inside and outside the drop.

a. Hydrodynamics modeling

In this section, we present the equations describing the axisymmetric motion of a nonoscillating spheroidal water drop falling under the influence of gravity. Figure 1 shows the schematic diagram of the numerical do-

main, where \(a\) and \(b\) are the lengths of the major and minor semi-axes of the spheroid, respectively, which are determined from the relationships of Chuchottaworn and Asano (1986) and from experimental data (Clift et al. 1978). The physical domain is discretized in the form of a network of nodes (or nodal points). The discretization was done by using 2997 nodes inside the drop and 5400 nodes outside the drop. In this approach, we have run the model using a 10^{-6}\text{s} step time. Flow fields are obtained by numerically solving the time-dependent Navier–Stokes equations of motion for viscous, incompressible, axisymmetric flow, which can be expressed with the Helmholtz formulation (streamfunction \(\psi\) and vorticity \(\omega\) in oblate spheroidal coordinates \((\xi, \eta)\) and in dimensionless form as a streamfunction equation,

$$\frac{1}{\cosh^2 \xi - \sin^2 \eta} \left( \frac{\partial^2 \psi}{\partial \xi^2} - \tanh \xi \frac{\partial \psi}{\partial \eta} + \frac{\partial^2 \psi}{\partial \eta^2} - \cot \eta \frac{\partial \psi}{\partial \xi} \right) = \omega, \quad (2)$$

and a vorticity equation,

$$\frac{\partial \omega}{\partial t} = \frac{4 \Phi \cosh^2 \xi}{\cosh^2 \xi - \sin^2 \eta} \left( \frac{\partial^2 \omega}{\partial \xi^2} + \frac{\partial^2 \omega}{\partial \eta^2} + \tanh \xi \frac{\partial \omega}{\partial \xi} + \cot \eta \frac{\partial \omega}{\partial \eta} \right) - 4 \Phi \cosh^2 \xi \frac{1 + \cot^2 \eta}{\cosh^2 \xi} \omega,$$

$$- \frac{2 \rho \Re(T) \cosh \xi \sin \eta \sinh (\cosh^2 \xi - \sin^2 \eta)}{\rho \cosh \xi \sin \eta (\cosh^2 \xi - \sin^2 \eta)} \times \left( \frac{\partial \psi}{\partial \xi} \frac{\partial \omega}{\partial \eta} - \frac{\partial \psi}{\partial \eta} \frac{\partial \omega}{\partial \xi} + \tanh \xi \frac{\partial \psi}{\partial \xi} - \cot \eta \frac{\partial \psi}{\partial \xi} \right)$$

$$- \frac{\omega_j}{\Re(T)} \frac{d \Re}{d \Re}, \quad (3)$$

where \(\Phi = \mu / \mu_0\) is the liquid side and \(\Phi = \rho / \rho_0\) is the gas side, \(\mu\) is the dynamic viscosity, \(\rho\) is the density, \(v\) is the kinematic viscosity, \(\xi\) is the radial coordinate, \(\eta\) is the tangential coordinate, \(\xi\) is the value of \(\xi\) at the surface of the spheroid, \(a\) is the major semiaxis length of the spheroid, \(U(t)\) is the particle velocity, \(\omega = \omega \sigma a / U(t)\) is the dimensionless vorticity, \(\psi = \psi U(t) a^{-1}\) is the dimensionless streamfunction, \(T = \mu \sigma a^2 (4 a^2 \rho)^{-1}\) is the dimensionless time, \(\Re(t) = 2 \nu \sigma U(t) / \nu_0\) is the Reynolds number, the starred quantities are dimensional, and \(x = i\) or \(0\) refers to inside or outside the drop, respectively.

Outside the drop, where the gradients are steep, the choice of spheroidal coordinates facilitates the formulation of the spheroidal boundary conditions and the use of a finite difference method. In addition, the exponential properties of the spheroidal coordinates produce a fine lattice near the surface for the spheroid in general and near the tips in particular, and a coarse lattice far away from the surface (Masliyah and Epstein 1970).

![Fig. 1. Schematic diagram of the field of computation.](image-url)
Equations (2) and (3) are constrained inside and outside the drop with the following boundary conditions.

1) Far from the drop at the outer boundary ($\xi = \xi_o$) undisturbed parallel flow is assumed:
   \[
   \omega_o = 0, \quad \psi_o = \frac{1}{2} \sin^2 \xi \cosh^2 \xi_o \sinh^2 \xi_o. \quad (4)
   \]

2) Along the axis symmetry ($\eta = 0, \pi$) we have
   \[
   \omega = 0, \quad \psi = 0; \quad \omega_o = 0, \quad \psi_o = 0. \quad (5)
   \]

3) Across the gas–liquid interface ($\xi = \xi_i$) we have the following relations:

   negligible material transfer,
   \[
   \psi_i = 0, \quad \psi_o = 0; \quad (6)
   \]

   continuity of tangential velocity, and
   \[
   \frac{\partial \psi_i}{\partial \xi} = \frac{\partial \psi_o}{\partial \xi}; \quad (7)
   \]

   continuity of tangential shear stress,
   \[
   \frac{\mu \left( \frac{\partial^2 \psi_i}{\partial \xi^2} - \tanh \xi_i \frac{3 \cosh^2 \xi_i - \sin \eta \frac{\partial \psi_i}{\partial \xi}}{\cosh^2 \xi_i - \sin^2 \eta \frac{\partial \psi}{\partial \xi}} \right)}{\mu_o} = \left( \frac{\partial^2 \psi_o}{\partial \xi^2} - \tanh \xi_o \frac{3 \cosh^2 \xi_o - \sin \eta \frac{\partial \psi_o}{\partial \xi}}{\cosh^2 \xi_o - \sin^2 \eta \frac{\partial \psi}{\partial \xi}} \right). \quad (8)
   \]

4) Liquid and gas vorticity at the interface are given, respectively, by
   \[
   \omega_i = \frac{\mu_o}{\mu} \left( \omega_o - \frac{2 \sinh \xi_i \cosh^2 \xi_o}{\sin \eta (\cosh^2 \xi_o - \sin^2 \eta)^2} \frac{\partial \psi_o}{\partial \xi} \right) + \frac{2 \sinh \xi_o \cosh^2 \xi_o}{\sin \eta (\sinh^2 \xi_o + \cosh^2 \eta)^2} \frac{\partial \psi_i}{\partial \xi}; \quad (9)
   \]
   \[
   \omega_o = \frac{1}{\cosh \xi_o \sin \eta \sinh^2 \xi_o + \cosh^2 \eta} \left( \frac{\partial^2 \psi_i}{\partial \xi^2} - \tanh \xi_i \frac{\partial \psi_i}{\partial \xi} \right). \quad (10)
   \]

The solutions of the vorticity Eq. (3) need the particle velocity $U(t)$, which appears in the Reynolds number $Re(t)$. For spherical drop accelerating under the influence of gravity, the particle equation in nondimensional form is expressed as

\[
\frac{dRe}{dT} = \frac{8a^3}{\mu_o} (\rho_1 - \rho_o) g - \frac{3}{4} \frac{a}{r_e} C_D Re^2, \quad (11)
\]

where $g$ is the gravitational acceleration, $r_e$ is the equivalent radius of a sphere of the same volume as the drop, and $C_D$ is the total drag coefficient.

The total drag coefficient $C_D$ is computed from the equation proposed by Berry and Pranger (1974) assuming that a water drop in air has a radius that a spherical drop of the same volume would have

\[
Re = \exp\{-3.126 + 1.013 \ln(C_D Re^2) - 0.01912[\ln(C_D Re^2)]^2\}, \quad (12)
\]

where $Re$ ranges between 0.1 and 3650 and the term $C_D Re^2$ between 2.4 and 107.

The dimensionless radial and tangential velocity components are related to the streamfunction in spherical coordinates by the following relations:

\[
\begin{align*}
  u_i &= -\frac{\cosh^2 \xi_i - \sin \eta \frac{\partial \psi_i}{\partial \xi}}{\cosh \xi \sin \eta \cosh^2 \xi - \sin^2 \eta \frac{\partial \psi}{\partial \eta}} \frac{\partial \psi}{\partial \xi} \\
  u_\eta &= \frac{\cosh^2 \xi_i - \sin \eta \frac{\partial \psi_i}{\partial \xi}}{\cosh \xi \sin \eta \cosh^2 \xi - \sin^2 \eta \frac{\partial \psi}{\partial \eta}} \frac{\partial \psi}{\partial \eta}.
\end{align*} \quad (13)
\]

Equations (2) and (3) together with the above boundary conditions are evaluated numerically with several combinations of parameters. The equations of motion inside and outside the drop are solved by finite difference approximations, with central differencing for all derivatives. The elliptic streamfunction equations are solved iteratively, the parabolic vorticity equations are solved by means of the alternating direction implicit method, so the efficient Thomas algorithm is used, and the particle equation is solved by the Runge–Kutta algorithm (Press et al. 1988).

The present model developed for spheroidal water drops falling freely in the air was first tested for $E = 1$ with the results obtained by Caussade and Saboni (1992), that is to say, the same as spherical drops. The comparison is done for different drop radii. We have observed that both analyses  yield the same results, which suggests that the present model is valid for spherical and spheroidal water drops and gives accurate numerical solutions.

Figure 2 shows the streamlines $\phi^*$, and the lines of constant vorticity $\omega^*$ of the flow inside and outside an oblate water droplet at its terminal velocity in the air are given in Fig. 2 for a radius of 300 $\mu$m ($Re = 100$) and an aspect ratio of $E = 0.995$ (5% oblateness). It is important to observe that both internal and external flows show asymmetry. Of note is the importance of the secondary recirculation in the rear of the drop. The main vortex in the water drop is driven by the tangential stress exerted by air flowing downstream over a large part of the drop. In this case, the stress exerted by the circulation in the trailing vortex is sufficiently large to cause the creation of a small secondary vortex inside the drop that moves in the opposite direction of the main vortex. Here it is important to underline that this phenomenon has also been observed by Leclair et al. (1972) but for a drop with a radius of about 500 $\mu$m ($Re = 300$). This difference between the surface velocity calculated in the spheroid by our model and the value obtained in the sphere by the model of Leclair et al. (1972) is small for $Re = 100$ and increases with larger Reynolds numbers due to smaller aspect ratios.

Figure 3 compares the interfacial shear stress distri-
Fig. 2. Streamlines and vorticity contours inside and outside a circulating drop of an equivalent radius of 300 μm (Re = 100) and $E = 0.995$.

Distributions for $E = 1$ (spherical shape) and $E = 0.974$ (oblate shape) of a 620-μm radius drop. The influence of a slight oblateness concerns a large part of the drop surface between the two angle positions of $20^\circ$ and $120^\circ$. For an angle coordinate of the order of $55^\circ$ the difference is roughly 15%. The oblateness increases the interfacial convection and enhances the convective motion inside the drop.

Figure 4 shows the factor relating surface tangential velocity distribution in a spheroid, $U_\infty$, to the value in the corresponding sphere, $U_\infty$, with a Reynolds number in the range of 100–420. The difference between the surface velocity in the spheroid and the value in the sphere is small for Re = 100 and increases with the Reynolds number due to smaller aspect ratios. The surface velocity reaches a maximum at $60^\circ$ and changes sign at $135^\circ$ for Re = 100 and $114^\circ$ for Re = 420°.

The shape and size of the drop significantly affect the
drag coefficients. The form drag coefficient $C_{DP}$ and the skin friction drag coefficient $C_{DF}$ are numerically obtained through integration of the distribution of surface pressure and vorticity as follows:

$$C_{DP} = \frac{8}{Re} \tanh \xi \int_0^\eta \omega(\xi) \sin^2 \eta \, d\eta$$

$$C_{DF} = \int_0^\eta P \sin^2 \eta \, d\eta. \quad (14)$$

The total drag coefficient $C_D$ is the sum of the form and skin drag coefficients. Values of $C_{DP}$, $C_{DF}$, and $C_D$ are presented in Table 1, which compares the drag coefficients for spheroidal drops (the present model) with the corresponding ones for spheres (Leclair et al. 1972). One can see that there is no difference between the spheroid drag and the sphere drag as small drops remain spherical in shape at moderate Reynolds numbers; drops used here have an aspect ratio ranging from about 0.996 for $Re = 100$, to 0.967 for $Re = 420$.

### b. Mass transfer

In this section, we present the partial-differential equations describing gas absorption by spheroidal water drops freely falling under the influence of gravity. In this model, resistance to mass transfer is considered to occur in both the liquid and gas phases so that Eq. (1) must be solved for both inside and outside the drop.

Outside the drop, we assume that no chemical reaction between the diffusing gas and air takes place and, thus, $R_s = 0$. In this case, Eq. (1) in spheroidal coordinates and in nondimensional form is written as

$$\frac{\partial C_g}{\partial T_s} = -\frac{\cosh \xi \sinh \eta}{2} \left[ \frac{\partial}{\partial \xi} \left( \cosh \xi \sinh \eta \sqrt{\cosh^2 \xi - \sin^2 \eta} U_{\xi\xi} C_g \right) \right. \left. + \frac{\partial}{\partial \eta} \left( \cosh \xi \sinh \eta \sqrt{\cosh^2 \xi - \sin^2 \eta} U_{\eta\eta} C_g \right) \right]$$

$$+ \frac{\cosh \xi \sinh \eta}{\cosh^2 \xi - \sin^2 \eta} \left[ \frac{\partial^2 C_g}{\partial \xi^2} + \frac{\partial^2 C_g}{\partial \eta^2} + \tanh \xi \frac{\partial C_g}{\partial \xi} + \cot \eta \frac{\partial C_g}{\partial \eta} \right]. \quad (15)$$

where $C_g = c_g/c_{g\infty}$ is the gas dimensionless concentration outside the drop; $c_{g\infty}$ is the gas concentration far away from the drop; $T_s = D_s t a^2$ is the dimensionless time; $D_s$ is the SO$_2$ molecular diffusivity in the air; $D_s = 0.136 + 5.64 \times 10^{-4} \theta$ (°C); $t$ is the time; $Pe_s = 2aU_s/D_s$ is the gas side Peclet

### Table 1. Total drag coefficients for fluid sphere and spheroid.

<table>
<thead>
<tr>
<th>Re</th>
<th>Sphere</th>
<th>Spheroid</th>
<th>Sphere</th>
<th>Spheroid</th>
<th>Sphere</th>
<th>Spheroid</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.49</td>
<td>0.50</td>
<td>0.59</td>
<td>0.59</td>
<td>1.08</td>
<td>1.09</td>
</tr>
<tr>
<td>300</td>
<td>0.34</td>
<td>0.33</td>
<td>0.29</td>
<td>0.28</td>
<td>0.63</td>
<td>0.61</td>
</tr>
<tr>
<td>420</td>
<td>0.23</td>
<td>0.24</td>
<td>0.27</td>
<td>0.26</td>
<td>0.50</td>
<td>0.51</td>
</tr>
</tbody>
</table>
number; \( U_\lambda = u \xi \lambda / U_a \) and \( U_\eta = u \eta / U_a \) are the dimensionless tangential and radial velocity components of the gas phase flow, respectively; and \( g \) represents the continuous or external gas phase.

Inside the drop, the gas forms a number of different chemical components (see the appendix for SO\(_2\)). In order to model the total sulfur in the drop, the convective-diffusion equation must be solved for each chemical species. According to Walcek and Pruppacher (1984), it is sufficient to calculate the total sulfur concentration, since it was found that chemical conversions between the various species of sulfur formed inside the drop did not modify the total S uptake, so that the term source RA in Eq. (1) is canceled on the liquid side. Then, the convective-diffusion equation applied inside the drop is expressed in spheroidal coordinates and in a nondimensional form as follows:

\[
\frac{\partial C}{\partial \gamma} = -\frac{\cosh \xi \cdot \text{Pe}_l}{2 \cosh \xi \sin \eta (\cosh^2 \xi - \sin^2 \eta)} \times \left[ \frac{\partial}{\partial \xi} (\cosh \xi \sin \eta \cosh^2 \xi - \sin^2 \eta U_\lambda C_l) \right. \\
+ \frac{\partial}{\partial \eta} (\cosh \xi \sin \eta \cosh^2 \xi - \sin^2 \eta U_\eta C_l) \left. \right] \\
+ \frac{\cosh^2 \xi \gamma}{\cosh^2 \xi - \sin^2 \eta} \times \left[ \frac{\partial^2 C_l}{\partial \xi^2} + \frac{\partial^2 C_l}{\partial \eta^2} + \tanh \xi \frac{\partial C}{\partial \xi} + \cot \eta \frac{\partial C}{\partial \eta} \right],
\]

(16)

where \( C_l = c_l / c_{init} \) is the instantaneous sulfur dimensionless concentration inside the drop; \( c_{init} \) is the saturation concentration of SO\(_2\) in water; \( T_l = D_l / l^2 \) is the dimensionless time; \( \text{Pe}_l = 2aU_\lambda / D_l \) is the liquid side Peclet number; \( D_l = 1.66 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \) is the diffusivity of SO\(_2\) in water; \( U_\lambda = u \xi \lambda / U_a \) and \( U_\eta = u \eta / U_a \) are the dimensionless tangential and radial velocity components of the liquid phase flow, respectively; and \( l \) represents the dispersed or liquid phase.

Equations (15) and (16) are coupled together and solved numerically with the following specified initial and boundary conditions.

1) The liquid is initially assumed to be clean:

\( T > 0: \)

\[
\xi \geq \xi_b, \quad 0 \leq \eta \leq \Pi; \quad C_l = 0.
\]

(17)

2) The SO\(_2\) concentration is initially assumed to be uniform in the gas environment:

\( T = 0: \)

\[
\xi_a \leq \xi \leq \xi_b, \quad 0 \leq \eta \leq \Pi; \quad C_g = 1.
\]

(18)

3) Very far from the drop, the gas concentration is uniformly mixed:

\( T > 0: \)

\[
\xi \geq \xi_a, \quad 0 \leq \eta \leq \Pi; \quad C_g = 1.
\]

(19)

4) Along the axis of symmetry, we have

\( T > 0: \)

\[
0 \leq \xi \leq \xi_a, \quad \eta = 0; \quad \frac{\partial C_l}{\partial \eta} = 0
\]

(20)

5) At the gas–liquid interface, it is assumed that the radial mass flux is continuous,

\( T > 0: \)

\[
\xi = \xi_a, \quad 0 \leq \eta \leq \Pi;
\]

\[
D_l \text{C}_{init} \frac{\partial C_l}{\partial \xi} = D_g \text{C}_g \frac{\partial C_g}{\partial \xi},
\]

(22)

and that a local saturated equilibrium is established between the liquid and the gas phases within each time step:

\( T > 0: \)

\[
\xi = \xi_a, \quad 0 \leq \eta \leq \Pi;
\]

\[
\text{C}_{li} = \frac{\sqrt{K_{li} K_{g}}}{{\text{C}_{init}}^2} (\text{C}_g)^{1/2} + \frac{K_{g} \text{C}_g}{\text{C}_{init}} - \text{C}_g,
\]

(23)

where \( \text{C}_{li} \) and \( C_g \) are the dimensionless concentrations in the liquid and gas phases at the drop surface, respectively; and \( K_{li} \) and \( K_g \) are the equilibrium constants for dissolved SO\(_2\) and dissociated H\(_2\)SO\(_4\) in water, respectively, which are given in the appendix. Gas and liquid concentrations near the surface of the drop are computed using the gas–liquid equilibrium relations and Taylor approximations of the convective-diffusion equations inside and outside the drop. In this model we assume that the outer surface of the drop is always saturated.

The resulting system of equations was solved numerically by an IBM RS 6000 work station. The diffusion-convection equations are strongly influenced by the large value of the Peclet number. The predominance of the convective term gives them a marked hyperbolic nature. For this reason, we adopt a predictor-corrector finite difference procedure based on the MacCormack (1981) method, which is well adapted to solve this kind of problem. The method is stable and second-order accurate in space and time. The first step predicts a new solution and uses a one-sided difference to approximate the first derivative and a centred derivative for the second derivative. The second step corrects the predicted values with an opposite one-sided difference for the first derivative and a centred derivative for the second derivative.

In Fig. 5, an example of the internal and external...
concentration fields for a 420-μm droplet as it falls through an environment containing a 2-ppm sulfur dioxide concentration for different absorption times is presented. These curves represent the numerical solutions to the full convective-diffusion equation inside and outside the drop. We can see the influence of the internal convective pattern on the concentration profiles. The gas is carried from the rear of the drop by induced external flow and it is convected into the drop by internal return circulation. The angle of injection depends on the intensity of the secondary vortex. In correlation with this concentration increase in the rear part of the drop, we clearly observe a decrease in the external concentration of the gas in the wake of the drop in the interfacial region. As the sulfur concentration inside the drop increases, the surface of the drop comes to equilibrium and the external concentration becomes uniform and equal to the initial concentration of SO₂. This process is very important and confirms that the convective-diffusion equation must be solved inside and outside the drop in order to take into account resistance to mass transfer in both the liquid and gas phases. Most of the models proposed in the literature do not consider the external concentration field pattern, so that the concentration inside the drop is not accurately predicted. The numerical fields presented also show the great influence of the deformation of the drop on the flow fields as well as the concentration fields inside and outside the drop. For high initial gas concentrations (in this case, resistance to mass transfer occurs only in the liquid phase) this wake rapidly disappears, the gas concentration becomes uniform up to the drop surface, and the drop surface comes to equilibrium rapidly.

Figure 6 shows the concentration gradients with respect to radial distance at the surface in the gas phase as a function of the angle at various times. We observe that the position of the minimum of the concentration gradient in the rear of the drop moves continuously to reach the position of the separation angle of the motion at the surface of the drop. As time increases, the gradient of the SO₂ concentration in the gas phase decreases rapidly, the concentration outside the drop becomes uniform and equal to the initial concentration of SO₂ in the gas phase, and then the concentration inside the drop becomes saturated.

Figure 7 shows the concentration profiles inside and outside spherical and spheroidal water drops, 90° from the forward direction of the drop across the liquid–gas interface for a 0.06-s absorption time. One can see oscillatory solutions in the interior of the drop that are greater near the interface region. This profile inside the drop is due to the strong effect of the main and the secondary circulation. Low negative values can be generated by the numerical scheme, but they are very low (see Fig. 7) and only occur in the liquid phase, near the interface, during the first few hundredths of a second. For this example the initial SO₂ concentration in the gas phase is about 10% volume/volume (v/v). In this case, the concentration gradient in the gas phase rapidly disappears and gas concentrations become uniform up to the drop surface, so that a steady-state solution of the convective-diffusion equation exists in the gas phase and the concentration of SO₂ outside the drop can be modeled by the film theory (Whitman 1923). However, for the absorption of trace gas into water, the convective-diffusion equation must also be solved numerically in the gas phase to take into account the resistance to diffusion in the gas domain limited to about 2 drop radii away from the surface of the drop, and after this the concentration becomes uniform. It is important to underline that for a high initial SO₂ concentration, spheroid drops absorb more than sphere drops for absorption times less than 0.05 s.

Figure 8 shows the nondimensional average concentration inside spherical and spheroidal water drops as a function of absorption time for various drop sizes and initial concentrations of sulfur dioxide. We observe that smaller drops absorb more sulfur than larger drops and the characteristic absorption times vary as drop sizes change. Also, this figure shows that the characteristic absorption times are longer at lower initial SO₂ concentrations than at higher ones because a high initial gas concentration of sulfur inside the drop is converted into the bisulfite form, so that the total sulfur concentration inside the drop relative to the gas concentration outside the drop is smaller at higher initial SO₂ concentrations. In this figure, one can see that spheroidal and spherical water drops (less than 1 mm in diameter) absorb sulfur at the same rate because deformation is very small.

Figure 9 shows an example of the nondimensional average concentration inside a drop of 420-μm radius as a function of the absorption time for different aspect ratios. We observe that concentrations inside the drop are smaller at higher aspect ratios (drops are spherical) than at lower ratios, so that deformed oblate drops approach saturation much faster than spherical drops. From the numerical simulations of sulfur concentrations inside spherical and spheroidal water drops, the average sulfur concentrations in a spheroid can be closely deduced from the average concentrations on a sphere by the following relation:

$$
\frac{C_{\text{spheroid}}}{C_{\text{sphere}}} = 14.89 \exp(-2.7E),
$$

(24)

where $E$ is the aspect ratio, defined by the relation (Clift et al. 1978)

$$
E = \left(1 - \frac{9}{16} \frac{r_e U_e^2}{\rho_w \sigma}\right)^{1/2}
$$

(100 μm < $r_e < 500$ μm),

(25)

where $\rho_w$ is the water density ($\rho_w = 1$ gm cm⁻³), $r_e$ is the equivalent radius of the drop in cm, and $\sigma$ is the surface tension ($\sigma = 72.75$ dynes cm⁻¹).
Fig. 5. Numerical visualisation of the concentration fields for a 420-μm droplet as it falls through a 2-ppm concentration of SO₂.
3. Theoretical approach for large drops

When the convective-diffusion equation is solved for drops larger than about 1 mm in diameter, the solution became unstable after iterations with the required small time step of about $10^{-6}$ s it is impossible to apply to the present model. In order to predict the mass transfer coefficients inside large drop sizes, we propose a parametric model based on the scaling of interfacial agitation, taking into account the effect of turbulent mixing and oscillation inside the drops.

It is important to remember that for drops larger than 1 mm in diameter, a number of parameterized models of the internal mass transfer coefficients have been developed. Unfortunately, low correlation was generally observed with experimental data. The reasons are certain. First, the experimental data confirm that the predicted results using models that assume steady circulation do not exhibit the physical phenomenon involved in mass transfer. Second, these models do not take into account the deformation characteristics of the drop. Consequently, the length and the velocity scales appearing in proposed models are not representative of the processes involved.

As a result of these investigations, it seems necessary
to reconsider the scaling of the mass transfer process, keeping in mind the important role played by agitation in the liquid near the liquid–gas interface of the deformed nonoscillating drop.

The liquid film coefficient is influenced by the ordering of the water molecules into the surface film and, although a large number of studies have been devoted to interfacial turbulence, little is known about how the fluid motion acts to break down the film and enhance the transport process. The liquid film coefficient has been measured for jet flows, bubble flows, falling films, stirred vessels, and open channel flows (Theofanous et al. 1974; Caussade et al. 1990).

It is important to note that all the models postulate that the transfer process is done across a rigid surface. Thus, this concept conflicts with the physical phenomena involved in mass transport. The importance of this problem has led to many models that take into account turbulence in the liquid and at the interface.

Therefore, whatever the concepts, local absorption models may be expressed as

\[ K_i = K(U_s, l_s, D_l, \nu, \sigma), \]  

(26)

where \( K_i \) is the liquid phase mass transfer coefficient; \( D_l \) the gas molecular diffusivity in liquid; \( \nu \) the kinematic viscosity of the liquid; \( \sigma \) the tension forces; and \( U_s \) and \( l_s \) the interfacial turbulence liquid velocity and length scales, respectively.

Using dimensional considerations, Eq. (26) can be expressed as

\[ \frac{K_i}{U_s} = \text{Re}_s^\alpha \text{Sc}_s^\beta \text{We}_s^\gamma, \]  

(27)

where \( \text{Re}_s \) is the local Reynolds number, \( \text{Re}_s = U_l l_s/\nu_s \); \( \text{Sc} \) is the Schmidt number, \( \text{Sc} = \nu_s/\sigma D_l \); \( \text{We}_s \) is the local Weber number, \( \text{We}_s = \rho_l U_l^2 l_s/\sigma \); and \( \alpha, \beta, \) and \( \gamma \) are constants to be determined from theoretical and experimental investigations.

It is interesting to point out the following points.

1) Most absorption models propose that the mass transfer coefficient varies with a \(-\frac{1}{2}\) exponent of the Schmidt number (Levich 1962; Fortescue and Pearson 1967; Davies 1972; Ueda et al. 1977; Henstock and Hanratty 1979). Recently, Jähne et al. (1987) and Caussade et al. (1990) showed that the Schmidt number exponent is equal to \(-\frac{1}{2}\) for rather strong interfacial stress and a clean interface whereas it is equal to \(-\frac{1}{2}\) when the interface behaves closer to a wall.

2) Almost all of the models do not consider the Weber number, which characterizes the action of surface tension, except those of Levich (1962), Davies and Ting (1967), and Davies (1972), where the Weber number exponent is taken to be equal to \(-\frac{1}{2}\).

3) The Reynolds number exponent varies from \(-\frac{1}{2}\) to \(\frac{1}{2}\). A value of \(\alpha = \frac{1}{2}\) corresponds to the large-eddy models (Fortescue and Pearson 1967; Ledwell 1984).

A value of \(\alpha = -\frac{1}{2}\) corresponds to the small-eddy models (Lamont and Scott 1970; Tsacyanannis et al. 1978).

We notice from a review of the literature that the basic difference between parametric absorption models concerns the choice of the characteristic scaling of interfacial turbulence.

In many of the parametric models the velocity scale is taken to be the interfacial liquid friction velocity, which is defined by the following relation:

\[ u_\theta = \left( \frac{\rho_l^{1/2}}{\rho_g^{1/2}} \right)^{1/2}, \]  

(28)

where \( \rho_l \) is the water density and \( \tau \) is the interfacial shear stress.

Absorption studies of oxygen, carbon dioxide, and helium in a concurrent stratified gas–liquid flow have shown the fundamental role played by the following parameters in the transfer phenomenon.

1) The interfacial friction velocity, which is well correlated with the absorption coefficient (Caussade et al. 1990).

2) The characteristic length scales of the waves near the sheared interface: interfacial roughness (Tsacoyannis 1976), wavelength (Baleix 1984), and interfacial-level fluctuations (Caussade et al. 1990).

3) The Schmidt number is fairly well related to the mass transfer coefficient. This has been confirmed by simultaneously studying the absorption of carbon dioxide and helium, two gases that present a large contrast in molecular diffusivity (Caussade et al. 1990).

The main conclusion in the literature is that the gas absorption process is strongly related to the structure of the liquid flow, which can be characterized by the interfacial liquid friction velocity. The role of the Schmidt number, which usually characterizes the physical properties of the gases, is accurately predicted.

It is clear that whatever the type of two-phase flow, the interfacial liquid friction velocity seems to be a good velocity scale to take into account for the effect of interfacial shear stress. Reasoning by analogy, this concept can be applied to parameterize the agitation process that appears inside large drops.

Contributions to the total force exerted on a body moving through a fluid are made by the tangential stress at the body surface integrated over that surface, and by normal stress. These forces in the case of a fluid sphere falling freely in the atmosphere are, respectively, the friction drag and the pressure drag, since the first one is a consequence of viscosity or friction in the fluid, and the second results from pressure force, which depends strongly on the shape of the body.

It is common practice to discuss drag of moving bluff bodies in the form of values of the dimensionless drag coefficient defined as (Batchelor 1988)
where $D$ is the total drag (a retarding force), $\rho_s$ is the air density, $U_*$ is the drop terminal velocity, and $A$ is the area of the projection of the body on a plane normal to the stream. So, it is easy to deduce the interfacial shear stress from the following equation:

$$\tau_s = \frac{1}{2} \rho_s U_*^2 C_D.$$ (30)

The drop terminal velocity is calculated by integrating the motion equation deduced from the force balance between drag force and gravitational acceleration for the drop-air system. Then, for a spheroidal drop accelerating under the influence of gravity, the motion equation can be expressed as

$$\frac{dU}{dt} = \frac{\rho_l - \rho_s}{\rho_l} g - \frac{3 \rho_s a^2}{8 \rho_l r_e^2} C_D U_*^2,$$ (31)

where $g$ is the gravitational acceleration; $a$ is the major semiaxis of the spheroid; $r_e$ is the equivalent radius of the drop; and $C_D$ is the total drag coefficient integrating both the pressure and vorticity effects through the form drag and the skin friction coefficients, respectively.

The minor and the major semiaxis of the spheroid are determined from the aspect ratio ($E = b/a$) using the following equation of Pruppacher and Pitter (1971):

$$E = 1.050 - 0.131 r_e \quad (0.5 < r_e < 4.5 \text{ mm})$$ (32)

and assuming that a water drop in the air has an equivalent radius of the drop that a spherical drop of the same volume would have, so that $(4/3) \pi a^3 b = (4/3) \pi r_e^3$. The total drag coefficient is computed from Eq. (12) of Berry and Pranger (1974).

In the absence of local measurements, the droplet diameter $d_e$ seems to be a good length scale, which is a characteristic of the large convective cells appearing inside drops falling from rest under the influence of gravity.

In the context of analysis of the literature presented in the previous paragraph, the choice of the two scales ($u_*$ and $d_e$) that point out the large-eddy model concept of Fortescue and Pearson seems to be the best way to model the liquid mass transfer coefficient in the case of large drops.

Then, the liquid mass transfer coefficient is given by the following equation:

$$K_l = \frac{D}{u_*}.$$ (33)

where $Re_s$ is the interfacial Reynolds number, $Re_s = 2r_u u_s / \nu_l$; $Sc$ is the liquid Schmidt number, $Sc = \nu_l / D_l$; $u_*$ is the interfacial liquid friction velocity; $\nu_l$ is the liquid kinematics viscosity; $D_l$ is the water–SO$_2$ diffusivity; $r_e$ is the equivalent radius of the drop; and $\omega$ is a constant to be determined from experimental results.

In other words, the proposed correlation of the mass transfer coefficient for drops larger than 1 mm is then of the following form:

$$K_l = \omega \left( \frac{D u_h}{d} \right)^{1/2},$$ (35)

with

$$u_h = U_* \left( \frac{1}{2} \frac{\rho_s}{\rho_l} C_D \right)^{1/2}.$$ (36)

Therefore, it is easy to deduce at any given time the values of the interfacial friction velocity and, correspondingly, the liquid mass transfer coefficient.

Figure 10 shows the comparison between the calculated liquid Sherwood number ($Sh = 2r_s K_l / D_s$) of the present study, the parameterized models of the literature, and the experimental data of Garner and Lane (1959), Kaji et al. (1985), Walcek et al. (1984), Altwicker and Lindhjem (1988) and Amokrane (1993). The comparison is carried out using either sulfur dioxide or carbon dioxide. The experiments correspond to normal conditions (1 Pa, 20°C), so that the liquid mass transfer co-
Table 2. Liquid mass transfer coefficients.

<table>
<thead>
<tr>
<th>Models</th>
<th>$K_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Handlos and Baron (1957)</td>
<td>$0.00375U/(1 + \rho_l/\rho_g)$</td>
</tr>
<tr>
<td>Angelo et al. (1966)</td>
<td>$2 / \sqrt{\Pi} \left(fD \left(1 + \epsilon + 3\epsilon/8\right)\right)^{1/2}$</td>
</tr>
<tr>
<td>Ruckenstein (1967)</td>
<td>$2 / \sqrt{\Pi} \left(UD\right)^{1/2}$</td>
</tr>
<tr>
<td>Walcek et al. (1984)</td>
<td>$-\frac{d}{6\omega} \ln \left(\frac{3}{8} \sum_{i=1}^{N} A_{i \omega} \exp \left(-\lambda_i \frac{64D_l}{d_2}\right)\right)$</td>
</tr>
</tbody>
</table>

Efficiencies are computed with an estimated value of 550 for the calculated Schmidt number. One can see that the experimental data and the parameterized models from the literature conflict because most of them utilize the drop velocity as the characteristic scale as shown in Table 2.

The model of Handlos and Baron (1957), which was developed for liquid spheres with the assumption that the transfer process is due to the internal turbulent movement, seems to slightly underestimate the mass transfer rate of droplets less than 2 mm in diameter; however, for larger diameters this model considerably overestimates the experimental results (up to 300% or 400%).

The model of Angelo et al. (1966) uses drop oscillation frequency defined by the following relation of Lamb (1932): $f = \frac{48 \sigma d^3 \rho_l (2 + 3 \rho_l/\rho_g)}{\pi^2}$, where $\sigma$ is the surface tension; $d$ the droplet diameter; and $\rho_l$ and $\rho_g$ are the water and air density, respectively. This model overestimates the mass transfer rate to drops smaller than 4 mm in diameter and seems to work best over the 4-mm diameter drop.

The model of Ruckenstein (1967), which postulated that the concentration of the drop is homogeneous and the transfer process occurs along a very thin boundary layer adjacent to the gas–liquid interface, considerably overestimates the mass transfer rate for the entire drop size range.

The model of Walcek et al. (1984) showed three regimes of droplet absorption:

1) Molecular diffusion regime (radius $r$ less than 20–70 $\mu$m). For extremely small drops (with a radius less than a few tens of $\mu$m), mass transfer can be explained by molecular diffusion into a stagnant spherical drop. From classical theories of diffusion in spheres, the time constant to establish saturation is about $T = D/\alpha^2 = 0.057$ (non-dimensional time).

2) Molecular diffusion and spherical vortex internal circulation regime (20–70 $\mu$m < $r$ < 500–800 $\mu$m). As drops begin to develop appreciable fall speeds, an internal circulation develops, probably somewhere between a 10- and 100-$\mu$m radius. This internal circulation significantly increases the rate of mass transfer into the droplet, but the flow is laminar, and the rate-limiting process governing the time constant for the absorption of mass is molecular diffusion perpendicular to the streamlines of the spherical vortex that becomes established inside the falling droplet. The time constant for establishing equilibrium is considerably smaller ($T = 0.0216$), about a factor of 2.6 shorter than for a stagnant sphere.

3) Turbulent diffusion and spherical vortex internal circulation ($r > 500–800$ $\mu$m). For very large drops (radius greater than about 1000 $\mu$m), timescales for mass absorption are significantly smaller by about a factor of 18 from the above regime. The authors found time constants for mass absorption/desorption ($T = 0.0012$), which are about 18 times smaller than the above regime and 48 times smaller than the stagnant sphere.

However, we observe that the present parametric model [Eq. (34)] suggested in this section shows an adequate correlation when $\omega = 1$.

Through $C_D$, balanced by the ratio of the gas density to the liquid density, the interfacial liquid friction velocity takes into account the influence of pressure and vorticity on the drag. In other words, the interfacial friction velocity is a good interfacial scale to parameterize the mass transfer process. The velocity fields inside and outside the drop are strongly related to the liquid viscosity. Now, referring to Eq. (35), the mass transfer coefficient appears to be independent of the liquid viscosity. In fact, this apparent independence is simply due to the value of the exponents in Eq. (33). This is the reason why it is important to discuss the results in terms of the Sherwood number, for spheroidal drops by the following correlation:

$$\text{Sh} = \text{Re}^{0.5}\text{Sc}^{0.5}.$$  \hspace{1cm} (37)

One can see that the spheroid liquid Sherwood number can be closely estimated by multiplying the sphere liquid Sherwood number by 1.25. Then at higher drop radii, the parametric model developed for large spherical drops (Amokrane et al. 1994) can be used to simulate the gas mass transfer behavior to large spheroidal drops by introducing an effective liquid Sherwood number of about 1.25 times the sphere Sherwood number.

4. Experimental study

In order to have new series of experiments under carefully controlled laboratory conditions to validate the theoretical models of sulfur dioxide mass transfer in freely falling water drops, an experimental device was constructed at the Institut de Mécanique des Fluides de
To evaluate the theoretical models, three broad categories of experiments were performed: reversible absorption, irreversible absorption, and desorption.

Experiments were carried out using a 5-m rain shaft, illustrated in Fig. 11. This device consisted of an arrangement of four main Plexiglas parts.

One part is a closed compartment where doubly distilled deionized water drops are generated. The larger drops (diameter greater than 1 mm) are obtained with calibrated hypodermic needles, using a constant upstream water pressure. The smaller drops (radii less than 500 μm) are produced using a modification of the droplet generator described by Abbott and Cannon (1972). Drop radii are determined by collecting a known number of drops and weighing them on a precise scale.

The second part of the apparatus is a cylindrical tube (0.1 m in diameter), where drops accelerate under the influence of gravity after generation. The acceleration distance was about 2.7 m and allows drops of radii less than 400 μm to reach their terminal velocity. The acceleration distance is determined using the method of Wang and Pruppacher (1977). Drops of more than 400 μm do not reach their terminal velocity; their sorption of SO₂ is simulated with the parametric model proposed for the large drops.

Drops are allowed to fall in the acceleration tube, after which they pass through absorption columns of variable lengths from 0.2 to 1.0 m. Before each experiment, a gas mixture with the desired SO₂ concentration ranging between 0.1% and 10% (v/v) was introduced into the absorption section. The SO₂ concentration is set at the desired value by regulating the volumetric flow rates of sulfur dioxide and air with calibrated rotameters. The SO₂ and air mixture is rendered homogeneous by circulation with a gas mixer. Concentrations of SO₂ are measured by circulating the gas through a Rosemount Binos 4a UV spectrometer. The absorption compartment has two gates, one at the top and the other at the bottom. They are closed before each experiment to introduce the gas mixture and then opened to allow a known number of drops to fall.

After various absorption contact times, drops are collected in a special glass cup placed at the lower part of the absorption column. The cup initially contains a known volume of doubly distilled deionized water for analysis. In accordance with the experimental works of Kaji et al. (1985) a kerosene film is used between the collector and the absorption column to prevent the SO₂ gas mixture from flowing down to the collector and contaminating the collected drops.

To determine the absorption rate of SO₂ into the drops, the concentration of H₃O⁺ is analyzed by using a pH-meter Orion 901 with an Orion 91-05 glass electrode. Then the total amount of sulfur in the solution is computed from hydrolysis equilibrium reactions of sulfur dioxide equations in water (see appendix). The total sulfur in the aqueous solution is also determined by three additional methods.

In the first method, the sulfur solution is converted by H₂O₂ into a sulfuric acid solution, which is titrated with a standard solution of NaOH using a mixture of bromocresol green and methyl red as an indicator. In the second method, the sulfur is also converted by oxidation with H₂O₂ to a solution of H₂SO₄. The conductivity is measured by using a Tacussel CD 60 resis-
tive meter, which is calibrated by means of a set of standard sulfate solutions. In the third method, sulfur concentrations are determined by adding 0.1 M sodium tetrachloromercurate (II) to the solution. The presence of sulfur is based on the red-violet color produced when pararosaniline in dilute hydrochloric acid and formaldehyde are added to the collector solution. The intensity of the resulting color is determined by means of a Sekomam PRIM C spectrophotometer operating at 0.56 μm. The spectrophotometer is calibrated by means of a set of standard solutions.

Before each set of experiments, the air in the shaft is purified and set at the desired temperature and humidity by recirculating it with a fan through a temperature regulator, an air humidifier system, and filters. Humidity control is obtained with saturated salt solutions. The advantage of this technique lies in its minimal humidity fluctuation as long as temperatures are in the range of 5°–30°C (Larbi et al. 1995). For determining the drop temperature, the relative humidity and the temperature are continually measured by hygrometers and thermocouples. The temperature in the shaft is between 14° and 25°C and the relative humidity is between 70% and 80% regulated with ammonium sulfate. The temperature of the drops is computed using the method described by Beard and Pruppacher (1971). After each set of experiments, the air in the shaft is purged through a NaOH solution and replaced with clean air.

5. Results and discussion

a. Drop size

Photographs taken by a camera through a microscope after catching the drops in oil at the same time showed a system of quite uniformly sized drops. It can therefore be deduced that the equivalent radius of one drop is the average radius of drops caught in the same sample. Then, the average drop size is determined by collecting a known number of them and weighing them on a precise scale. The tuning parameter that characterizes the drop size is the Sauter radius, defined as

\[ a_{32} = \frac{\sum_{i=1}^{n} a_i^3}{\sum_{i=1}^{n} a_i}, \]  

where \( a_i \) is the equivalent radius and \( n \) is the measure number.

Figures 12 and 13 illustrate two examples of the frequency distribution or histogram of small and large drop radii. These figures confirm that the drops are uniform in size. In our cases, \( a_{32} = 359 \pm 20 \) μm for the small drops and \( a_{32} = 2295 \pm 20 \) μm for the large drops. The drop size distributions were monitored both at the top and at the bottom of the column. We have observed that the drop size changed insignificantly when the drops fell through the air column. This is a consequence of the rapid speed of their fall and the small residence times of the drops. In doing so, we assume that the flow fields inside a drop of 360 μm will differ only negligibly from the flow fields for drops of 360 ± 20 μm.

b. Absorption time

The characteristic absorption times of the drop are calculated by integrating the equation of motion of a water drop, which is deduced from the force balance between the drag force and gravitational acceleration for the drop-air system. The total drag coefficient is deduced from the equation proposed by Berry and Pranger (1974), assuming that a water drop in the air has the same radius as a spherical drop of the same volume would have.

Figure 14 shows comparison between the experi-
mental data of Wang and Pruppacher (1977) and the present theoretical prediction of the fall speeds of freely falling water drops. Very high correlation is found, thus justifying the assumptions that the residence times of the drops can be accurately determined from the drop velocity by numerically integrating the particle equation of motion.

c. Average concentrations

1) REVERSIBLE ABSORPTION

A prediction of the average concentration of the chemical forms inside small drops is obtained by integrating the local concentrations over each volume:

$$\langle C \rangle = \frac{\int V C(\xi, \eta) \, dV}{\int V \, dV}, \quad (39)$$

where $V$ is the drop volume, and $C(\xi, \eta)$ are the dimensionless sulfur concentration fields obtained at a given time and location by numerical solutions to the convective-diffusion equation coupled to the Navier-Stokes equations inside and outside the drop. The integral in Eq. (39) is approximated by the alternating extended trapezoidal rule.

A comparison of the full convective-diffusion model with the experimental average drop concentrations as a function of absorption time is shown in Fig. 15 for a 300-μm equivalent radius drop as it falls through a 0.19% and a 10% (v/v) mixture of SO$_2$. The models are initialized with zero concentration of SO$_2$ in the drops falling into a well-mixed gas at a specified SO$_2$ concentration in the absorption column. Concentrations very far from the drop are maintained at the initial SO$_2$ concentration by mixing the gas in the absorption column.

We observe that our experimental data compares favorably with the values predicted. It is important to point out that the predicted values obtained for spherical drops are at the same rate for the spheroidal drops in which the ratio aspect is small and drops of about 300 μm oscillate in shape about 0.996 times the ratio aspect. In these figures one can see that, in addition to studying the absorption, the boundary conditions can be modified to describe desorption behavior, which is represented by the dashed lines. For the desorption process, which was simulated in the experiments of Walcek et al. (1984), the external boundary conditions are set at zero concentration of SO$_2$.

In order to test larger drop sizes, the average concentration of total sulfur dioxide is deduced by integrating the following expression of the flux of gas at the interface:

$$V \frac{d(C_g)}{dt} = SK(C_l - \langle C \rangle), \quad (40)$$

where $K$ is the liquid mass transfer coefficient; $C_g$ is the liquid interface concentration; $t$ is the time; and $V$ and $S$ are the volume and the surface of the spheroid, respectively. Also, $V = (4/3)\pi a^2 b; S = 2\pi a^2 + \pi(b^2/2)\ln(1 + e/(1 - e)); e$ is the eccentricity, $e = (a^2 - b^2)^{1/2}/a$; and $a$ and $b$ are the major and minor semiaxes, respectively.

Then, the instantaneous concentration inside a large drop is obtained by integrating Eq. (40) as follows:

$$\langle C \rangle_{n+1} = C_{n+1}^o - [C_o^o - \langle C \rangle^o] \exp \left[ -\frac{S}{V} K \Delta t \right], \quad (41)$$

where $\langle C \rangle_{n+1}$ is the average sulfur concentration in the drop at the time $(n + 1)\Delta t$; $C_o^o$ is the liquid interface concentration at the time $n\Delta t$; and $\Delta t$ is the time step.

Equation (41) needs the initial conditions, which are expressed as

$$t = 0, \quad \langle C \rangle^o = 0, \quad \text{and}$$

$$C_o^o = (K_{K}K_{g,e}V)^{1/2} + K_{g}C_{w,e}, \quad (42)$$

where $C_{w,e}$ is the initial SO$_2$ concentration in the gas phase, and $K_{g}$ and $K_{e}$ are the equilibrium constants for dissolved SO$_2$ and dissociated H$_2$SO$_3$ in water, respectively, which are given in the appendix.

The liquid interface concentration at the next time step is obtained from the gas surface concentration assuming that the drop is in a local saturated equilibrium with the gas at the drop surface:

$$C_{n+1}^o = (K_{g}K_{g,e}V_{p})^{1/2} + K_{g}C_{w,e}, \quad (43)$$

The gas surface concentration $C_{w,e}$ is computed from the film theory model (Whitman 1923), since the steady-state concentration fields are rapidly established in a thin layer of thickness $\delta$ around a falling drop and from
the assumption that at the gas–liquid interface the radial mass flux is continuous:

$$D_g \frac{C_{g,\infty} - C_{g,\infty}^{n-1}}{\delta_{g}} = K_{i}[C_{g}^{n} - \langle C_{g}^{n} \rangle^{+1}]$$

(44)

where $D_g$ is the molecular diffusivity of $\text{SO}_2$ in air.

The appropriate value for the film thickness is accurately obtained from the following relation of Beard and Pruppacher (1971):

$$\delta_{g} = \frac{d_{e}}{1.61 + 0.718 \text{Re}_{g}^{0.50} \text{Sc}_{g}^{0.33}},$$

(45)

where $\text{Sc}_{g}$ is the ratio of the viscosity of the gas phase to the diffusion of the gas through the gas phase ($v_{g}/D_{g}$) and $\text{Re}_{g}$ is the Reynolds number of the falling drop ($2r_{e}U_{e}/v_{g}$).

Average concentrations inside large drops as a function of absorption time are plotted in Fig. 16. Experiments were run for the absorption of 7.4% of $\text{SO}_2$ for a 2264-μm drop of radius, and 9.4% of $\text{SO}_2$ for a 2388-μm drop of radius.

In this category of experiments, drops have an oblate spheroidal shape with an aspect ratio of 0.76 and 0.73 for diameters of 4.5 and 4.8 mm, respectively. The results presented here show that our parametric model gives a good predictive solution in the case of reversible absorption.

2) IRREVERSIBLE ABSORPTION

The irreversible absorption experiments closely resemble the reversible absorption experiments described in the previous section, the difference being that drops are formed with hydrogen peroxide solution. In this fashion, the sulfur collected in this experiment is reversibly changed into sulfate, which does not escape from the drops. The concentration of $\text{H}_2\text{O}_2^+$ is also determined by pH measurements and hydroxide sodium titration. The sulfate concentration in the collected drops is computed from the relation given in the appendix. In addition, a conductimetric method is used to measure the sulfate in the solution. Drops with different radii are exposed to $\text{SO}_2$ gas concentrations for different absorption times. The initial concentration of hydrogen peroxide in the water was set at 0.2 M.

In order to compare the experiment with theory, our models are solved to include the effects of the oxidation of sulfur by hydrogen peroxide (for more details see the appendix).

Figure 17 shows the comparison between our experimental results and the predicted values for the absorption of 2.80% and 7.90% of $\text{SO}_2$ by a 328-μm radius drop. We observe that the experimental data have a very high correlation with those predicted by the complete model of the convection-diffusion equations, including the effects of the oxidation of sulfur by the hydrogen peroxide. One can see that drops created from the hydrogen peroxide solution absorb more than drops created from pure water, since the initial oxidant $\text{H}_2\text{O}_2$ concentration inside the drops alters the total absorption of $\text{SO}_2$.

For large drops, experiments were run for the absorption of 9.8% of $\text{SO}_2$ by a 1992-μm radius drop and of 0.99% of $\text{SO}_2$ by a 2308-μm radius drop. Results are summarized in Fig. 18. We observe that the present parametric model coupled with the oxidation mechanism of $\text{SO}_2$ by $\text{H}_2\text{O}_2$ fits the experimental data well. In these experiments the aspect ratio is about 0.79 and 0.75 for the 1992- and 2308-μm radii, respectively.

3) DESORPTION

In the desorption experiments the drops are produced with an initial concentration of $\text{SO}_2$ by bubbling a known flow rate of pure $\text{SO}_2$ gas through doubly distilled deionized water for a definite time. These drops are allowed to fall through the rain shaft for various times after their release to determine the rate of $\text{SO}_2$ desorption from the drops. After various desorption
times, drops are collected in a special cup placed at the bottom of the rain shaft. The cup initially contains a known volume of hydrogen peroxide solution. In this manner sulfur in the drops is converted immediately into sulfate. Sulfur concentration in the collected drops is determined using the methods described in the reversible absorption experiments.

The theory of SO₂ desorption from individual freely falling water drops is the same as the theory describing absorption. The difference lies in the external and initial boundary conditions. It is assumed that the drop is uniformly mixed with the SIV form of sulfur and the concentration of SIV in the external gas phase at a distance from the drop is set at zero at all times.

To test our models simulating this set of experiments, the fraction of the original concentration (the drop concentrations are normalized with respect to the initial sulfur concentration in the drop) as a function of fall time is plotted in Fig. 19 for small drops and Fig. 20 for large drop sizes.

We observed that the proposed theoretical models matched all the experimental data. We note that the mass transfer is accurately predicted by the Navier–Stokes and convection-diffusion equations for drops smaller than 1 mm in diameter. For drops larger than 1 mm in diameter, the proposed parametric model, based on an approach of interfacial transfer phenomenon through the interfacial friction velocity, takes into account the effects of the interfacial agitation in the liquid phase, the turbulent mixing and oscillation inside large drops, and yields good results. For this reason this type of model seems to be more realistic than other global models that have been proposed.

6. Conclusions

The purpose of this study is to contribute to a better knowledge of absorption phenomena and the prediction of mass transfer rates in the case of small and large spheroidal water drops falling in a polluted atmosphere. Our study shows the following conclusions.

1) Whatever the type of absorption and desorption experiments, our theoretical models for predicting SO₂ mass transfer rates into spheroidal water drops have satisfactorily been verified by our experimental data.

2) For drops of less than 1 mm in diameter, the absorption behavior may be described from numerical solutions to the convective-diffusion equation combined with numerically derived flow fields for both inside and outside the drops. These numerical solutions also show the great influence of the deformation of the drop on flow fields as well as the concentration fields inside and outside the drop. One of the main interests of these numerical solutions concerns the possibility of having a better understand...
standing of the absorption process and especially in the case of trace gases. This is clearly emphasized in the figure presenting the visualization of the concentration fields. For this figure, the outer limit of the gas domain is about 10 drop equivalent radii from the surface of the drop. However, we show an important gradient in the concentration just on the domain limited to about two drop equivalent radii away from the surface of the drop, and after this the concentration of the gas is uniform. This process exists and is very important as the resistance to diffusion also occurs outside the drop. For high gas concentrations outside the drop (in this case resistance to mass transfer occurs only in the liquid phase) this wake rapidly disappears and the gas concentration becomes uniform up to the drop surface. The numerical solutions also give information concerning the importance of the resistance to diffusion inside and outside the drop.

3) In the case of large drops and on the basis of our experimental results, it is evident that the parametric model based on the large-eddy renewal concept of Fortescue and Pearson, where the agitation process in the liquid phase near the interface is characterized by the interfacial friction velocity, provides very good results.

4) Another conclusion concerns the interesting capabilities offered by the 5-m rain shaft built and tested at the Institut de Mécanique des Fluides de Toulouse. Reversible and irreversible absorption experiments as well as desorption experiments have been performed, with the aim of testing the robustness of the models over a large spectrum of interfacial mass transfer conditions. These laboratory investigations, including some additional experiments, will also be used to test absorption experiments of others gases such as NOx, CO2, and insoluble organic gases.

5) Predicted and experimental values also give information on the variation of the average concentration of SO2 inside the drops over time.

6) This study allows one to understand the gas mass transfer problem for a single water drop falling through a mixture of SO2. More scientific efforts are necessary to simulate realistic atmospheric conditions such as mass transfer to different drop sizes with evaporation, condensation, breaking-up, or coalescence phenomena, as well as the effect of and chemical interactions due to the presence of many pollutants, insoluble aerosol particles, and surfactants.

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APPENDIX

Equilibrium Hydrolysis Reactions of Sulfur Dioxide

a. Equilibrium relations for sulfur dioxide in water

When sulfur dioxide is absorbed into water, the resulting equilibrium relations are expressed as follows:

\[
\text{SO}_2 + \text{H}_2\text{O} \Leftrightarrow \text{H}_2\text{SO}_3
\] (A1)

\[
\text{H}_2\text{SO}_3 + \text{H}_2\text{O} \Leftrightarrow \text{H}_3\text{O}^+ + \text{HSO}_3^-
\] (A2)

\[
\text{HSO}_3^- + \text{H}_2\text{O} \Leftrightarrow \text{H}_3\text{O}^+ + \text{SO}_3^-.
\] (A3)

The values of the equilibrium constants \(K_H\), \(K_1\), and \(K_2\) of reactions A1, A2, and A3 are given, respectively, by the following relations of Sillen (1964):

\[
K_H \text{ (moles/moles)} = \frac{[\text{H}_2\text{SO}_3]}{[\text{SO}_2]}
\]

\[
= 7.1 \times 10^{-4} \exp(3147/T) \quad \text{(A4)}
\]

\[
K_1 \text{ (moles/liter)} = \frac{[\text{HSO}_3^-][\text{H}_3\text{O}^+]}{[\text{H}_2\text{SO}_3]}
\]

\[
= 1.9 \times 10^{-5} \exp(2022/T) \quad \text{(A5)}
\]

\[
K_2 \text{ (moles/liter)} = \frac{[\text{SO}_3^-][\text{H}_3\text{O}^+]}{[\text{HSO}_3^-]}
\]

\[
= 2.4 \times 10^{-10} \exp(1671/T). \quad \text{(A6)}
\]

where \(T\) is the absolute temperature expressed in Kelvins.

The total sulfur concentration \([\text{SIV}]\) in water is expressed as

\[
[SIV] = [\text{H}_2\text{SO}_3] + [\text{HSO}_3^-] + [\text{SO}_3^-]. \quad \text{(A7)}
\]

After several manipulations from Eqs. (A4)–(A6), together with the conditions.

Condition of electroneutrality:

\[
[\text{H}_3\text{O}^+] = [\text{OH}^-] + [\text{HSO}_3^-] + 2[\text{SO}_3^-]; \quad \text{and (A8)}
\]

condition of water ionization:

\[
2\text{H}_2\text{O} \Leftrightarrow \text{H}_3\text{O}^+ + \text{OH}^- \quad \text{(A9)}
\]

the equilibrium constant of the water ionization is defined as

\[
K_w = [\text{H}_3\text{O}^+][\text{OH}^-] \quad \text{(i.e., } K_w = 10^{-14} \text{ at } 25\text{°C}) \quad \text{(A10)}
\]

and the total sulfur concentration as a function of pH of the solution is given by

\[
[SIV] = \frac{[\text{H}_3\text{O}^+]}{[\text{H}_3\text{O}^+]} \left\{ \frac{K_w}{[\text{H}_3\text{O}^+]} \right\} \times \left( \frac{[\text{H}_3\text{O}^+]^2 + K_1[\text{H}_3\text{O}^+] + K_1K_2}{K_1[K_2][\text{H}_3\text{O}^+]} + 2K_1K_2 \right). \quad \text{(A11)}
\]
The concentration of each species of sulfur in the water as a function of pH can be expressed as

\[ [\text{H}_2\text{SO}_3] = \left( \frac{[\text{H}_3\text{O}^+]}{[\text{H}_2\text{O}^+] - K_s} \right) \times \left( \frac{[\text{H}_2\text{O}^+]^2}{K_1[H_2\text{O}^+] + 2K_2} \right) \]  \hspace{1cm} (A12)

\[ [\text{HSO}_3^-] = \left( \frac{K_s}{[\text{H}_3\text{O}^+] - [\text{H}_2\text{O}^+]} \right) \left( \frac{[\text{H}_2\text{O}^+]^2}{K_1[H_2\text{O}^+] + 2K_2} \right) \]  \hspace{1cm} (A13)

\[ [\text{SO}_3^{2-}] = \left( \frac{K_s}{[\text{H}_3\text{O}^+] - [\text{H}_2\text{O}^+]} \right) \left( \frac{K_2[H_2\text{O}^+]}{[\text{H}_2\text{O}^+] + 2K_2} \right). \]  \hspace{1cm} (A14)

At the interface, the gas and the liquid saturation concentration are given by the following relations:

\[ [\text{H}_2\text{SO}_3]_{\text{sat}} = K_h C_{\text{g} e} \]  \hspace{1cm} (A15)

\[ 2K_2[\text{HSO}_3^-]_{\text{sat}} + K_h K_1 C_{\text{g} e} [\text{HSO}_3^-]_{\text{sat}} - (K_h K_2 C_{\text{g} e})^2 \]
\[ = 0 \]  \hspace{1cm} (A16)

\[ 4[\text{SO}_3^{2-}]_{\text{sat}} - \frac{K_h K_1 [\text{SO}_3^{2-}]_{\text{sat}}}{K_2} + 2K_h K_2 C_{\text{g} e} [\text{SO}_3^{2-}]_{\text{sat}} \]
\[ -K_h K_1 K_2 C_{\text{g} e} = 0, \]  \hspace{1cm} (A17)

where \( C_{\text{g} e} \) is the initial concentration of sulfur dioxide in the gas phase.

In the atmospheric conditions, pH values range between 4 and 5.5. For pH < 5.5, reaction (A3) may be neglected and the dominant sulfur forms in the water are \( \text{H}_2\text{SO}_3 \) and \( \text{HSO}_3^- \). In this case, the condition of electroneutrality becomes

\[ [\text{H}_3\text{O}^+] = [\text{HSO}_3^-]. \]  \hspace{1cm} (A18)

Thus, the total S concentration is given by

\[ [\text{SIV}] = [\text{HSO}_3^-] + [\text{H}_2\text{SO}_3] \]
\[ = \frac{[\text{H}_3\text{O}^+]^2 + K_s[H_2\text{O}^+]}{K_1}. \]  \hspace{1cm} (A19)

The total sulfur concentration in the water at the saturation point can be expressed as

\[ C_{\text{sat}} = K_h C_{\text{g} e} + (K_h K_2 C_{\text{g} e})^{1/2}. \]  \hspace{1cm} (A20)

When the drops pass through the rain shaft, they are collected in a cup initially containing a volume noted \( V_{\text{coll}} \) (ml) of distilled and deionized water. If we consider \([\text{SIV}]_{\text{drop}}\) and \([\text{SIV}]_{\text{coll}}\) as the total sulfur concentration in the drop and the collected solution, respectively, we obtain

\[ [\text{SIV}]_{\text{drop}} = \left[ \frac{V_{\text{coll}} + V_{\text{drop}}}{V_{\text{drop}}} \right] [\text{SIV}]_{\text{coll}}. \]  \hspace{1cm} (A21)

From Eq. (A19) and by measuring the pH = \(-\log[H_3O^+]\) of the collected solution, we have

\[ [\text{SIV}]_{\text{drop}} = \left[ \frac{V_{\text{coll}} + V_{\text{drop}}}{V_{\text{drop}}} \right] [\text{SIV}]_{\text{coll}}. \]  \hspace{1cm} (A22)

b. Equilibrium relations for sulfur dioxide in hydrogen peroxide solution

When sulfur dioxide is absorbed into the hydrogen peroxide solution, the sulfur S(IV) is converted to S(VI) as follows (Hoffman and Edwards 1975):

\[ \text{HSO}_3^- + \text{H}_2\text{O}_2 \leftrightarrow \text{H}_2\text{O}_2 + \text{HSO}_4^2^- \]  \hspace{1cm} (A23)

\[ \text{HSO}_3^- + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{O}_2 + \text{SO}_4^{2-}. \]  \hspace{1cm} (A24)

The equilibrium constant of Eq. (A24) is

\[ K_s (\text{moles/liter}) = \frac{[\text{SO}_4^{2-}][\text{H}_2\text{O}^+]}{[\text{HSO}_3^-]} \]
\[ = 0.012 \text{ moles/liter at 25°C}. \]  \hspace{1cm} (A25)

After some manipulations from Eq. (A25) together with the considerations that the total sulfur concentration \([\text{SIV}]\) is expressed as

\[ [\text{SIV}] = [\text{HSO}_3^-] + [\text{SO}_3^{2-}], \]  \hspace{1cm} (A26)

and the condition of electroneutrality is

\[ [\text{H}_3\text{O}^+] = [\text{HSO}_3^-] + 2[\text{SO}_3^{2-}], \]  \hspace{1cm} (A27)

we obtain the concentration of S(VI) as a function of pH of the solution:

\[ [\text{SIV}] = \frac{[\text{H}_3\text{O}^+](K_s + [\text{H}_2\text{O}^+])}{2K_1 + [\text{H}_2\text{O}^+]]. \]  \hspace{1cm} (A28)

When the drops pass through the rain shaft, they are collected in a cup initially containing a volume of \( \text{H}_2\text{O}_2 \) denoted \( V_{\text{coll}} \) (ml). If we designate the total concentration in the drop and in the collected solution as \([\text{SIV}]_{\text{drop}}\) and \([\text{SIV}]_{\text{coll}}\), respectively, and \( V_{\text{drop}} \) the volume (ml) of the drops in the cup, we obtain from mass conservation of sulfur the following relation:

\[ [\text{SIV}]_{\text{drop}} = \left[ \frac{V_{\text{coll}} + V_{\text{drop}}}{V_{\text{drop}}} \right] [\text{SIV}]_{\text{coll}}. \]  \hspace{1cm} (A29)

Since \([\text{H}_3\text{O}^+]\) is measured in the collector by a pH meter and NaOH titration, \([\text{SIV}]_{\text{coll}}\) can be determined from Eq. (A28). An expression for \([\text{SIV}]_{\text{drop}}\) in terms of quantities measured in the experiment is given by

\[ [\text{SIV}]_{\text{drop}} = \left[ \frac{V_{\text{coll}} + V_{\text{drop}}}{V_{\text{drop}}} \right] \frac{[\text{H}_3\text{O}^+](K_s + [\text{H}_2\text{O}^+])}{2K_1 + [\text{H}_2\text{O}^+]]. \]  \hspace{1cm} (A30)

c. Oxidation of sulfur (IV) by hydrogen peroxide solution

In order to calculate the rate of oxidation of S(IV) into S(VI) by hydrogen peroxide, we use the formula given by Martin and Damschen (1981):
From the equilibrium relations and the condition for electroneutrality we deduce the concentration of hydrogen ions as function of [SIV] and [SVI]:

\[
[H_3O^+] = \frac{K_1}{[SIV]} + [SVI]\left(\frac{K_2}{[SIV][H_2O^+] + K_1}\right).
\]

(A32)

Starting calculus from the expression of the flux at the interface, the concentration of hydrogen ions is determined from Eq. (A33) and the conversion of S(IV) to S(VI) from Eq. (A32). New concentrations are then obtained and the operation is repeated for the desired time.

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