Experimental Study and Parameterization of Gas Absorption by Water Drops

H. Amokrane, A. Saboni, and B. Caussade
INP-ENSEEIHT, Institut de Mécanique des Fluides, CNRS, 31400 Toulouse, France

Liquid-phase mass-transfer coefficients are determined for the absorption of sulfur dioxide by water drops larger than 1.1 mm in dia. A local model based on the large eddy interfacial model proposed by Fortescue and Pearson (1967) is obtained by the characteristic interfacial scaling. In particular, the agitation process of the liquid phase in the interfacial region is characterized by the interfacial liquid friction velocity. Experiments of sulfur dioxide absorption and desorption from large individually free-falling water drops are also carried out in a 5-m rain shaft under various environmental conditions. These experimental results agree well with those from the local model characterizing the interfacial process in water drops greater than 1.1 mm in dia.

Introduction

Mass transfer between liquid drops and a continuous gas phase occurs in a large number of industrial processes and many engineering disciplines such as chemical and nuclear engineering, atmospheric sciences, environmental engineering, and so on. A number of mathematical models have been proposed and many experimental investigations have been carried out in the air-pollution control domain in order to provide a better understanding of the scavenging of trace gases in clouds, rain drops, and industrial wet scrubbers. Recent studies, however, have shown that numerous models for the prediction of mass-transfer coefficient into drops are not sufficiently trustworthy. This is particularly true for the absorption and desorption for gases of low solubility (in this case resistance to penetration occurs in the liquid phase). 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 the liquid mass-transfer coefficients.

For drops falling in a gas of high solubility (in this case resistance to penetration occurs in the external gas phase) a survey of published works (Kaji et al., 1985; Altwicker and Lindhjem, 1988) shows that there are a number of good numerical models and experimental correlations for the prediction of gas film mass-transfer coefficients around a fluid.

On the other hand, a great number of parameterized models often applied in chemical engineering and atmospheric sciences have been developed to predict the liquid mass-transfer coefficient. However, these models and experimental data are not in good agreement. It is of value to remind the reader of the principal models.

Kronig and Brink (1950) considered the concentration of dissolved substance to be the same at any point of a given streamline and to vary only from one streamline to the next. Their internal mass-transfer coefficient is deduced using the solution of the diffusion equation for stationary droplets.

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 conclusion has also been made by Walcek et al. (1984) on the sulfur dioxide 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 and to be consistent with the turbulent interior of water drops of this size. So, they have observed an oscillation of large drops ($d > 1$ mm) about their equilibrium shape with a frequency varying from 200 to 30 Hz for the smaller and the larger sizes respectively. It seems that the level of these frequencies, and thus the value of the effective diffusivity, are inconsistent with a turbulent process. It is our opinion that it would be preferable to talk in terms of an agitation process.

Handlos and Baron (1957) developed a theoretical model for liquid sphere with the assumptions that the transfer process is due to internal turbulent movements of the drop and the internal flow field is expressed by Hadamard's equation. This model is one of the most popular and readily used in chemical engineering and atmospheric sciences. However, theory and experimental data conflict, mainly in the case of large drops.

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) and Ruckenstein et al. (1971) 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 the Hill's vortex solution near the liquid surface.

Ramachandran (1985) postulated a model in which the internal flow field is expressed by the Hill's vortex with weak velocities less than 7.5 times the Hill's velocities.

It is important to underline that for drops larger than 1.1 mm in diameter, a number of experimental data have been developed but poor agreement was generally observed with the parameterized models of the internal mass-transfer coefficient.

Apart from these parameterized models in which a steady circulation is assumed, more recent numerical investigations have been developed for drops smaller than 1.1 mm in diameter which are almost perfectly spherical in shape. It is numerically well established that falling drops in air exhibit a vigorous internal circulation (Leclair et al., 1972; Pruppacher and Beard, 1970) and that such circulation significantly affects the transfer of chemical species across the surface and into the interior of a drop. Baboolal et al. (1981) and Caussade and Saboni (1991) have developed theoretical models for gas absorption by water drops, taking into account the presence of internal flow fields described by the numerical solution of the Navier Stokes equation of motion.

The first conclusion from this literature review search is that the experimental data confirm that the predicted results using models assuming steady circulation do not exhibit the physical phenomenon involved in the mass transport. The second conclusion is that the length and the velocity scales are respectively taken to be the diameter and the terminal velocity of the drop in most of these parameterized models which can be considered as models of "global" type.

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 the agitation in the liquid near the liquid-gas interface. For this we find it reasonable to consider an analysis of the theoretical work, first carried out by Whitman (1923), concerning mainly absorption in stratified or wavy flows. This analysis relates to various situations and is the subject of the following section.

The purpose of this article is to test a new "local" model to predict the internal mass-transfer coefficient for large drops. For this, we have carried out experimental investigations using a 5-m rain shaft. Predicted results and experimental data have been compared in the case of sulfur dioxide absorption and desorption from air by freely falling water drops.

Absorption Models of "Local" Type

The liquid film coefficient is influenced by the ordering of the water molecules into the surface film and, although a great amount 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, 1974).

It is important to remark that all the models postulate that the transfer process is made across a rigid surface. If this is not the case there will exist a conceptual conflict in relation to the physical phenomenon involved in the mass transport. The importance of the problem has led to many models taking into account the turbulence in the liquid and at the interface.

So, whatever the concepts, local absorption models may be written as:

$$K_L = K_L\,(U_s,\ I_s,\ D_L, \nu_L,\ \sigma) \tag{1}$$

K_L is the liquid phase mass-transfer coefficient, D_L is the gas molecular diffusivity in liquid, ν_L is the kinematic viscosity of the liquid, σ is the tension forces, and U_s and I_s are the interfacial turbulence liquid velocity and length scales, respectively.

Using dimensional considerations, Eq. 1 can be expressed as:

$$\frac{K_L}{U_s} = Re_s^{\alpha}\ Sc^{\beta}\ We_s^{\gamma} \tag{2}$$

Re_s is the local Reynolds number: $Re_s = U_s\ I_s/\nu_L$; Sc is the Schmidt number: $Sc = \nu_L/D_L$; and We_s is the local Weber number: $We_s = \rho_L\ U_s^2 I_s/\sigma$.

α, β and γ are constants to be determined from theoretical and experimental investigations.

It is interesting to underline the following points:

(1) Most absorption models proposed that the mass-transfer coefficient varies with $-1/2$ 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 $-1/2$ for rather strong interfacial stress and a clean interface whereas it is equal to $-2/3$ when the interface resembles a wall.

(2) Almost all of the models do not consider the Weber number which characterize 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 equal 1/2.

(3) The Reynolds number exponent varies from $-1/2$ to 1/2. $\alpha = 1/2$ corresponds to the large eddy models (Fortescue and Pearson, 1967; Ledwell, 1984). $\alpha = -1/2$ corresponds to the small eddy models (Lamont and Scott, 1970; Tsacoyannis et al., 1978).

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

On the other hand in many of these models the velocity scale is taken to be the interfacial liquid friction velocity which is defined by the following relation:

$$u_* = \sqrt{\frac{\tau_s}{\rho_L}} \tag{3}$$

Absorption studies of oxygen, carbon dioxide and helium in co-current 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 with the mass-transfer coefficient. This has been confirmed in studying simultaneously absorption of carbon dioxide and helium, two gases presenting a large contrast of molecular diffusivity (Caussade et al., 1990).

The main conclusion of the literature review 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 well predicted.

Liquid Mass-Transfer Coefficient for Large Drops

Present local approach

From the previous section, 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 the effect of interfacial shear stress. Reasoning by analogy, this concept can be applied to parameterize the agitation process which 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 the 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 of common practice to discuss drag of moving bluff bodies in the form of values of the dimensionless drag coefficient defined as (Batchelor, 1988):

$$c_f=\frac{D}{\frac{1}{2}\rho U^2 A} \tag{4}$$

where D is the total drag (a retarding force), and A is the area of the projection of the body on a plane normal to the stream ($A=\pi a^2$ for a sphere). So, it is easy to deduce the interfacial shear stress from Eq. 4 since $\tau_s=D/A$.

At high Reynolds numbers the total drag coefficient for a liquid sphere, which is in any event a function of Reynolds number alone, integrates both the pressure and vorticity effects respectively through the form drag, c_{DP}, and the skin friction, c_{DF}, coefficients: $c_f=c_{DP}+c_{DF}$. The viscous sphere ($\kappa=\mu_{water}/\mu_{air}=55$) has essentially the same drag as a rigid sphere, therefore: when $Re=100$, $c_{DP}=0.49$, and $c_{DF}=0.59$. And, as we can see, the dimensionless coefficient c_f has the convenient property of being of order of unity.

The terminal velocity, U, of a droplet accelerated under gravity (where added mass is neglected) is easily calculated integrating the equation of motion deduced from the force balance between the drag force and the gravitational acceleration.

The total drag coefficient, c_f, can be deduced 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 (it is important to underline that several other relations can be utilized):

$$-3.126+1.013\ln(c_f Re^2)-0.0192[c_f Re]^2=\ln(Re) \tag{5}$$

In this relation the Reynolds number range between 0.1 and 3550 and the term $c_f Re^2$ between 2.4 and 10^7.

Therefore, it is easy to deduce at any time the value of the interfacial friction velocity.

In the absence of local measurements, the droplet diameter, d, appears 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 the literature analysis presented in the previous paragraph, the choice of two scales (u_* and d) relate to the large eddy model concept of Fortescue and Pearson and this appears to be the best way to model the liquid mass-transfer coefficient in the case of large drops.

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

$$\frac{K_L}{u_*}=\omega Re_*^{-1/2}Sc^{-1/2} \tag{6}$$

Where ω is a constant to be determined from experimental data.

In terms of Sh (the liquid Sherwood number) our model can be expressed as:

$$Sh=\omega\, Re_*^{1/2}Sc^{1/2} \tag{7}$$

Where Re_* is the interfacial Reynolds number, $Re_*=(u_*d)/\nu_L$ and Sc is the Schmidt number, $Sc=\nu_L/D_L$.

In other words, the proposed correlation is of the following form:

$$K_L=\omega\left(\frac{D_L\,u_*}{d}\right)^{1/2} \tag{8}$$

with

$$u_*=U\sqrt{\frac{\rho_g}{\rho_L}\frac{c_f}{2}} \tag{9}$$

that is, for a 2 mm water drop falling in the atmosphere, $u_*\sim 10^{-2}U$.

Through c_f, balanced by the ratio of the gas density to the liquid density, u_* takes the contribution of pressure and vorticity to the drag into account. In other words, u_* depends on the forces acting at the interface of the drop, mainly the interfacial shear stress, which is responsible for the internal cir-

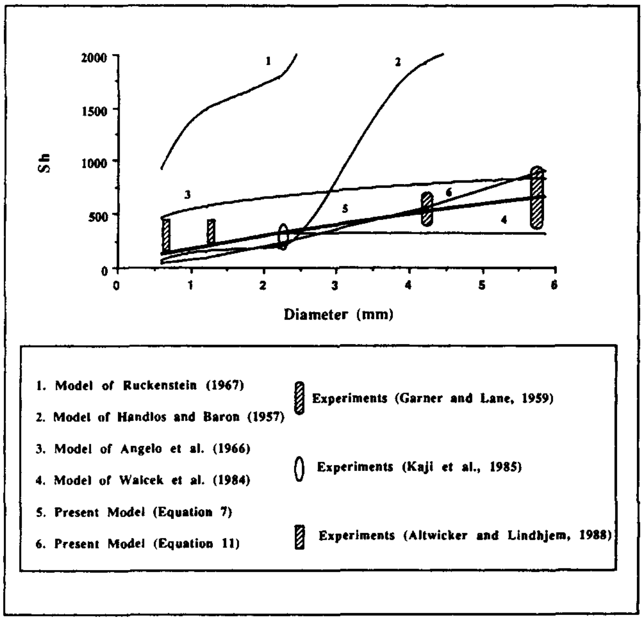

Figure 1. Liquid average Sherwood number vs. drop diameter.

culation. On the basis of these arguments, u_* seems to be a good interfacial scale to parameterize the mass-transfer process.

It is also of interest to test another approach to predict the mass-transfer rate to drops. As the tension forces are important at the drop interface one approach is to compare the interface with a solid boundary. In this case Caussade et al. (1990) have shown that the liquid mass-transfer coefficient varies with the 2/3 exponent of the Schmidt number:

$$K_L \sim u_* Sc^{-2/3} \tag{10}$$

In terms of Sh, this model can be expressed as:

$$Sh = \omega Re_* Sc^{1/3} \tag{11}$$

The velocity fields inside and outside the drop are strongly related to the liquid viscosity ν_L. Now, referring to Eq. 8, the mass-transfer coefficient appears to be independent of ν_L. As a matter of fact, this apparent independence is simply due to the value of the exponents in Eq. 7. This is the reason why it is important to discuss the results in terms of the Sherwood number.

Average concentration

Starting from the expression of the flux of a chemical species at the interface, we can write:

$$V \frac{\partial \langle C_1 \rangle}{\partial t} = S\, K_L\, [C_i - \langle C_1 \rangle] \tag{12}$$

Where S and V are respectively the surface area and the volume of droplets. Therefore, it is sufficient to know only these two quantities and to determine the mass-transfer coefficient from Eq. 8 to compute the average concentration in the droplets. However, drops larger than 500 μm in radius are not spherical; this is due to their shape deformation under the action of internal turbulence and oscillation. In this case the most reasonable analysis is to assume that the water drop has a radius that a spherical drop of the same volume would have.

So, regardless of the drop diameter, the integration of Eq. 12 leads to the following relation:

$$\frac{C_i - \langle C_2 \rangle}{C_i - \langle C_1 \rangle} = \exp\left[-\frac{6K_L}{d} (t_2 - t_1) \right] \tag{13}$$

Comparison with literature results

In order to evaluate these types of models, we compared them with those of the literature. Figure 1 shows also experimental data of Garner and Lane (1959), Walcek et al. (1984), Kaji et al. (1985), and Altwicker and Lindhjem (1988), which are the only experimental results published in the literature.

These experimental studies were carried out using either sulfur dioxide or carbon dioxide. But, in order to account for these results, we consider that the experimental conditions of these absorption experiments correspond to normal conditions of pressure and temperature (1 Pa, 20°C). For this reason, the liquid mass-transfer coefficients are computed with an estimate value of 550 for the calculated Schmidt number. All numerical values are summarized in Table 1.

Figure 1 and Table 2 show that the experimental data and the literature parameterized models conflict, indeed:

(1) The model of Angelo et al. (1966) overestimates the mass-transfer rate to drops smaller than 4 mm in diameter and seems to work best over the 4 mm diameter drop.

(2) The model of Handlos and Baron (1957) seems to slightly underestimate the mass-transfer rate to droplets less than 2 mm in diameter; however, for higher diameters this model considerably overestimates the experimental results (up to 300 or 400%).

(3) The models of Ruckenstein (1967) and Ruckenstein et

Table 1. Liquid Sherwood Numbers (Eqs. 7 and 11)

d (mm)	U (m/s)	Re_g	C_f	u_* (m/s)	Re_*	Sc	Sh (Eq. 7)	Sh (Eq. 11)
0.61	2.49	101	1.08	0.063	38	550	116	31
1.20	4.44	356	0.67	0.089	107	550	193	88
2.22	6.55	970	0.57	0.120	266	550	305	218
4.22	8.56	2,400	0.64	0.160	672	550	486	551
5.85	9.28	3,620	0.75	0.190	1,111	550	625	911

Table 2. Liquid Average Sherwood Numbers (Altwicker and Lindhjem, 1988)

d mm	Angelo et al. (1966) $\epsilon=0.3$	Angelo et al. (1966) $\epsilon=0.0$	Ruckenstein (1967)	Handlos & Baron (1957)	Exp.	Ref.
0.60	460	400	920	60	320 ± 80	Altwicker & Lindhjem (1988)
1.20	565	489	1,480	150	370 ± 30	Altwicker & Lindhjem (1988)
2.20	658	570	1,780	190	275 – 350	Kaji et al. (1985)
4.22	775	670	5,240	1,920	400 – 680	Garner & Lane (1959)
5.85	838	727	5,860	2,400	350 – 920	Garner & Lane (1959)

al. (1971) considerably overestimate the mass-transfer rate for the entire drop size range.

(4) The model of Walcek (1983) which predicts a steady-state Sherwood number of near 320 for all drop sizes and conditions is theoretically unsatisfying. This is certainly due to the use of an empirically determined effective diffusivity.

(5) On the other hand, the present local model (Eq. 7) suggested in this article appears to be theoretically satisfying in predicting the mass-transfer rate of drops larger than 1.1 mm in diameter. We observe that the theoretical curve with $\omega = 0.8$ matches the experimental data much better than the other models. This confirms the interest of absorption models based on the concept suggested by Fortescue and Pearson.

(6) Figure 1 shows that the second present model (Eq. 11) seems to work best for drops less than 4 mm in diameter with $\omega = 0.1$. However, it overestimates the mass-transfer rate for drops more than 4 mm in diameter.

We observe from this comparison that the local model based on the large eddy concept of Fortescue and Pearson with the interfacial liquid friction velocity as velocity scale, is a good tool to predict mass-transfer rates to drops from 1 to 6 mm in diameter. However, it is necessary to confirm this result on the basis of other experiments.

Another way to evaluate the present model (Eq. 7) is to study the evolution of the average concentrations of total sulfur dioxide vs. the exposure time.

Thus, we compare the present model (Eqs. 7 and 13) and the simplified model of Walcek (1983) with the experimental data of Walcek et al. (1984) concerning three broad categories of sulfur dioxide absorption/desorption by individual freely falling drops. In the first category, drops were allowed to come to terminal velocity, after which they passed through a chamber of variable length filled with various sulfur dioxide concentrations in air. After falling throughout a gas separating chamber consisting of a fluorocarbon gas, the drops were collected and analyzed for their total sulfur content in order to determine the rate of sulfur dioxide desorption. Figure 2 shows the average concentration of total sulfur dioxide absorbed by drops of 1,179 and 2,030 μm in radius vs. the absorption and desorption time. The second category of experiment closely resembled the first, except when the drops contain a various amount of hydrogen peroxide. In this case, sulfur absorbed by the drops becomes irreversibly changed into the sulfate form and the desorption cannot occur. Graphical results are presented in Figure 3 for two large drops. In the final category of experiments, drops initially saturated with S(IV) were allowed to fall through sulfur-free air to determine the rate of sulfur dioxide desorption. The results of these studies are summarized in Figure 4.

In the simplified model, Walcek (1983) used a combination of the approach of Kronig and Brink (1950) for the liquid phase and the film theory for the gas phase to explain mass

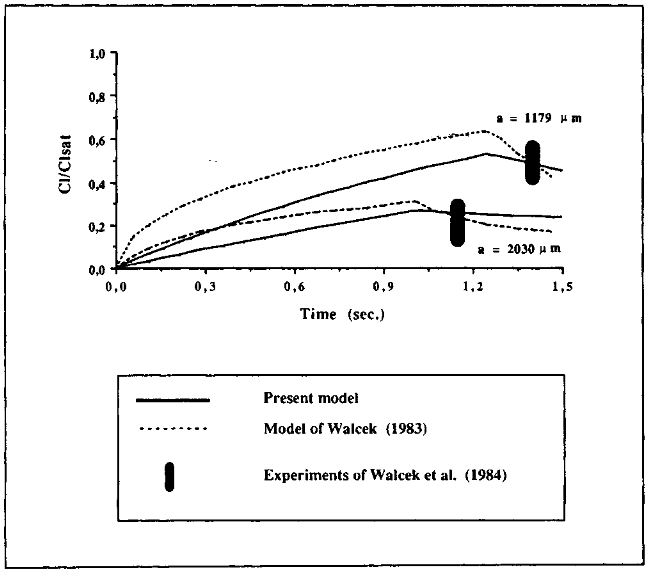

Figure 2. Theory vs. experiments in the case of SO_2 absorption into water drops.

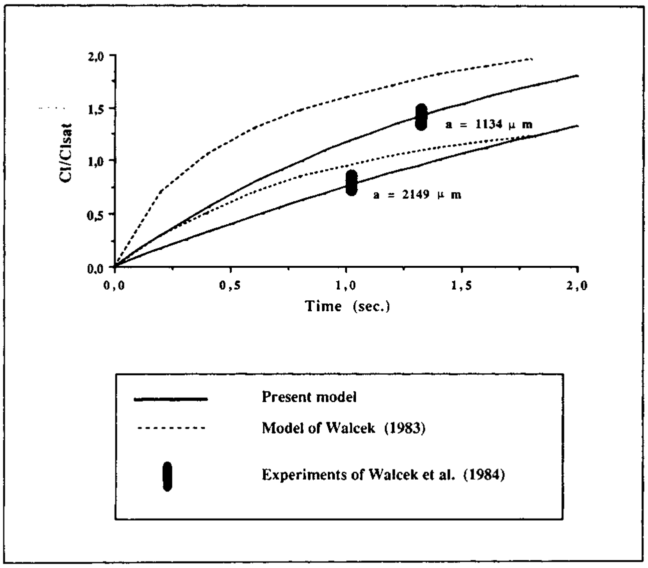

Figure 3. Theory vs. experiments in the case of SO_2 absorption into H_2O_2 drops.

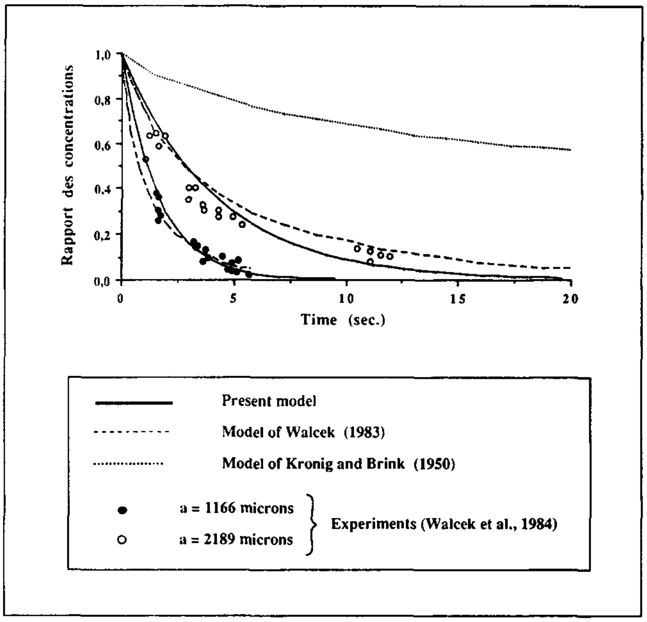

Figure 4. Theory vs. experiments in the case of SO_2 desorption from water drops.

transfer into large drops. However, in order to obtain agreement between theoretical predictions and experimental results, Walcek (1983) expected that some form of internal turbulent diffusion takes place dominating the previously assumed steady-state convection and molecular diffusion. The corresponding "eddy" diffusion coefficient was found empirically to have a value between 12 and 22 times the molecular diffusion coefficient.

In the case of the first category of experiments, Figure 2 shows that the simplified model of Walcek (1983) is in good agreement with the experimental data just as the present model. But, it is interesting to observe the large discrepancies predicted by the two models for shorter absorption times. In the case of the second category of experiments, Figure 3 shows large discrepancies between the simplified model and the data of Walcek et al. (1984). On the other hand, the present model fits very well the experimental data. In the case of the third category of experiments, Figure 4 shows that the two models are in good agreement with the experimental data of Walcek et al. (1984) but with a slight advantage to the present model.

Due to the lack of experimental results, it is impossible to conclude in favor of one of the models even if the model presented in this article appears to be better. This is the reason for which we have performed laboratory investigations at the IMFT. A 5-m rain shaft has been constructed with the aim being to test our described theory of sulfur dioxide absorption and desorption into or from individual freely falling large water drops.

Experimental Setup

Apparatus

Experiments are carried out using the 5-m rain shaft consisting of four main Plexiglass arrangements parts (0.1 m ID) with various lengths. Figure 5 shows a diagram of the experimental device. Drops of more than one millimeter in diameter are obtained with calibrated hypodermic needles and a constant upstream water pressure. Drops radii are determined by collecting a known number and weighting them on a precision balance. For the purpose of calculating the radius we assume that the drops are spheres. Before each set of experiments, the air in the shaft is purified and set at the desired temperature and humidity by recirculating it by a fan, successively 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 20 to 30°C (Larbi et al., 1990). For determining the temperature of the drops, the relative humidity and the temperature of the air in the shaft are continually measured, respectively, by hygrometers and thermocouples. Temperature in the shaft is between 14 and 25°C. Relative humidity is established between 50 and 60%. The temperature of drops is computed using the method described by Beard and Pruppacher (1971). After each set of experiments, the air in the shaft is purged in sodium hydroxide solution. In order to evaluate the theoretical model under experimental laboratory conditions, three broad categories of experiments are performed.

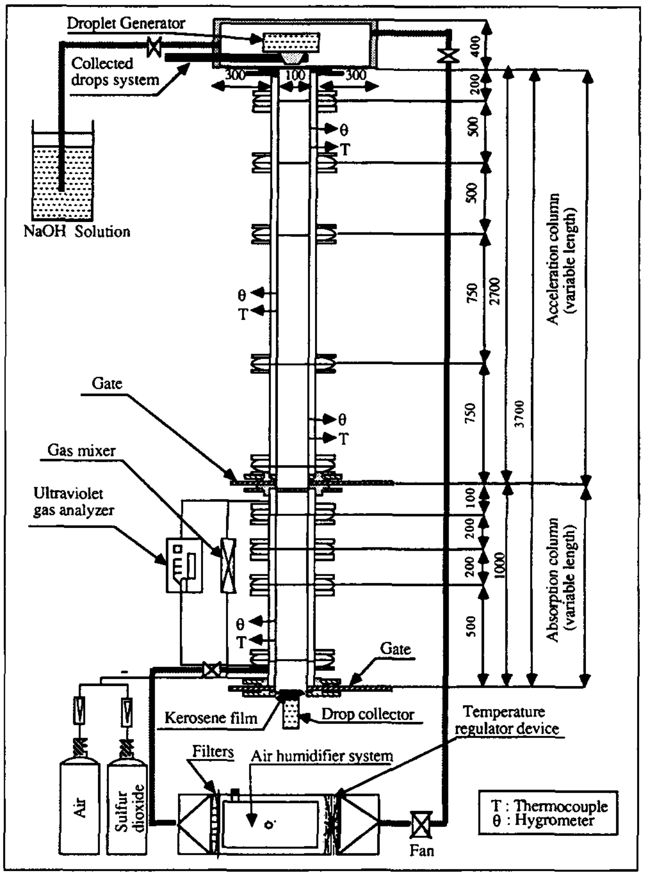

Figure 5. Experimental apparatus for studying sulfur dioxide absorption/desorption by water drops.

Distances are in mm.

Experimental procedure

Reversible Absorption. The drops are allowed to fall in the acceleration tube. An absorption column of various lengths is used. Before each experiment, a gas mixture with desired SO_2 concentration in air ranging between 2,000 ppm and 50% (v/v) is introduced into the absorption section. The SO_2 concentration is set at the desired value by regulating the volumetric flow rates of sulfur dioxide and air with calibrated rotameters. The gas mixture of SO_2 and air is rendered homogeneous by circulation with a gas mixer. The concentration of SO_2 gas is measured by circulating the gas through a Rosemount Binos 4a ultraviolet 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 bottom of the rain shaft. The cup initially contains a known volume of doubly distilled deionized water for analysis. A kerosene film is used between the collector and the absorption column to prevent the SO_2 gas mixtures from flowing down to the collector and contaminating the collected drops. To determine the absorption rate of SO_2 into drops, the concentration of H_3O^+ is analyzed by pH measurements, and the amount of sulfur in solutions is computed from equations given in Appendix A. The total sulfur in aqueous solutions is also determined by three additional methods. In the first method, the sulfur solution is converted by H_2O_2 into a sulfuric solution which is titrated with a standard solution of NaOH. In the second method, the sulfur is also converted by oxidation with H_2O_2 to a solution of H_2SO_4. The conductivity is measured by using a Tacussel CD 60 resistivemeter, which is calibrated by means of a set of standard sulfate solutions. In the third method, the amount of sulfur is determined by adding 0.1 M sodium tetrachloromercurate (II) to the solution. The determination of the sulfur is based on the red violet color produced when pararosaniline in a dilute hydrochloric acid and formaldehyde are added to the collector solution. The intensity of the resulting color is determined by means of a Secomam PRIM C spectrophotometer operating at 560 nm. The spectrophotometer is also calibrated by means of a set of standard solutions.

Irreversible Absorption. The irreversible absorption experiments closely resemble the first category of experiments. The difference being that the drops are formed with hydrogen peroxide solution. In this fashion, the sulfur collected in this experiment is irreversibly changed into sulfate form which cannot escape from the drops. The concentration of hydrogen peroxide is also determined by pH measurements and hydroxide sodium titration. The sulfate concentration in the collected drops is computed from the relation given in Appendix B. In addition, a conductimetric method is used to measure sulfate in solution. The apparatus is calibrated using standard sulfate solutions.

Desorption. The drops are produced with an initial concentration of sulfur dioxide ranging between 0.5 and 1.0 mole l^{-1} by bubbling a known flow rate of pure sulfur dioxide gas through doubly distilled deionized water for a definite time. Various drop sizes are used in these experiments. These drops are allowed to fall through the rain shaft for various times after their release to determine the rate of sulfur dioxide desorption from the drops. After various desorption contact times, drops are collected in a special cup placed at the bottom of the rain shaft. The cup initially contains a known volume about 25 ml of hydrogen peroxide. In this fashion the sulfur in the drops is immediately converted into sulfate. Sulfur concentration in the collected drops are determined using the methods described in the irreversible absorption experiments.

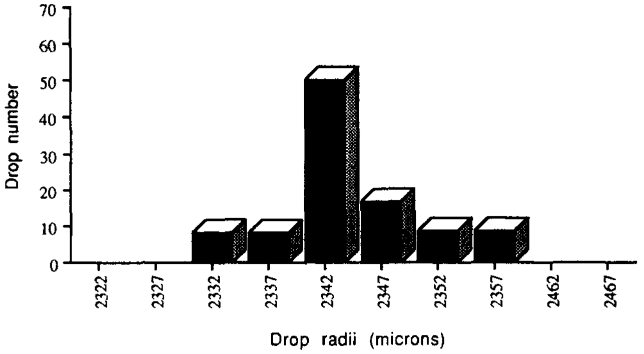

Figure 6. Frequency distribution of drop radii.

Results and Discussion

Drops size

The photographs which are taken by means of a camera through a microscope after catching the drops in oil show a system of quite uniformly sized drops. We can deduce that the equivalent radius of one drop is the average radius of drops caught in the same sample. Thus, the average drop size is determined by collecting a known number and weighing them on a precision balance. Drop radius is computed using the assumption that the drops are spheres.

In Figure 6, we illustrate an example of the frequency distribution or histogram of drop radii.

The absolute error of the equivalent radius is given by:

$$\Delta a_i = \frac{a_i}{3}\left[2\frac{\Delta M}{M} + \frac{\Delta N}{N} + \frac{\Delta \rho}{\rho}\right] \tag{14}$$

where a_i is the average radius of the drops collected in the same sample, M, N, and ρ are respectively weight, number, and density of the collected drops and ΔM, ΔN and $\Delta \rho$ are the corresponding absolute errors.

It is established that the drop size changes insignificantly while the drops fall through the air column. This is a consequence of the large fall speed and the small fall length, that is referring to Figure 6, $a_i = 2{,}344 \pm 20\ \mu m$.

With regard to the tuning parameter to characterize the drop size, the Sauter radii is used.

$$a_{32} = \frac{\sum_{i=1}^{n} a_i^3}{\sum_{i=1}^{n} a_i^2} \tag{15}$$

where a_i is the equivalent radius and n is the measure number. In our case, we have: $\Delta a = 20\ \mu m$ and $a_{32} = 2{,}344\ \mu m$.

Absorption and desorption time

The absorption and desorption time of the drop is calculated by integrating the equation of motion of a water drop through

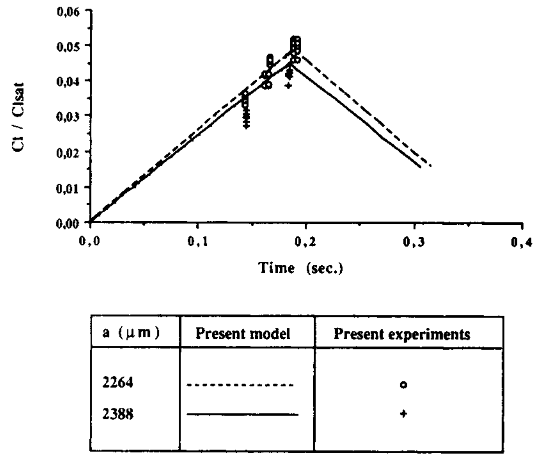

Figure 7. Average concentration inside drops as function of the absorption and desorption time.

the total drag coefficient deduced from Eq. 5. The comparison between the experimental data of Wang and Pruppacher (1977) and the present theoretical prediction of the fall speed of a freely falling water drop is excellent.

Average concentrations.

Reversible Absorption. Figure 7 shows the average concentration of total sulfur dioxide absorbed vs. the absorption and desorption time. These experiments are run with drop radii of 2,264 and 2,388 μm. We observe that our local model fits well our experimental data with $\omega = 0.8$.

Irreversible Absorption. Drops with equivalent radii of 1,992 and 2,294 μm are exposed to sulfur dioxide gas concentrations for different absorption times. The concentration of hydrogen peroxide in the water is set at 0.2 molar. In order to compare the experiment with theory, our theoretical model is solved to include the effects of oxidation of sulfur by hydrogen peroxide (see Appendix). In Figure 8, we observe that the experimental results are in very good agreement with the values predicted by the local model with $\omega = 0.8$.

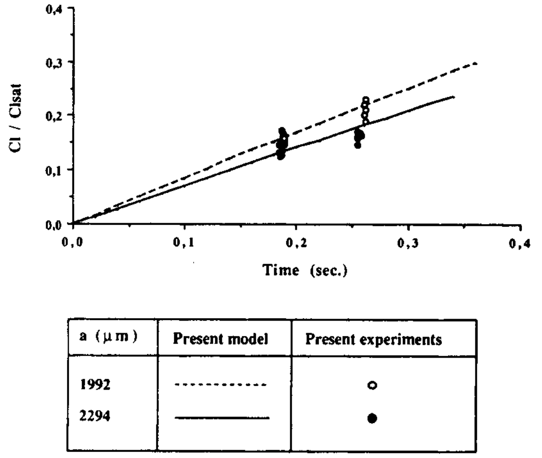

Figure 8. Average concentration as function of the absorption time with hydrogen peroxide as oxidizing agent inside drops.

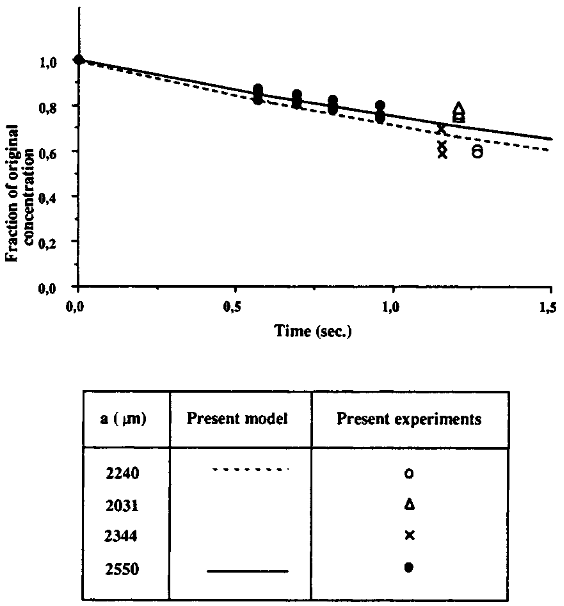

Figure 9. Variation of the fraction of the initial concentration in a freely falling drop as a function of the exposure time.

Desorption. To determine the rate at which sulfur dioxide is desorbed in air from individual freely falling water drops, the fraction of original sulfur dioxide concentration as a function of fall time is plotted in Figure 9. We observe that the proposed local model matches more accurately all the experimental data, with $\omega = 0.8$.

In these experiments, regardless of the length we use, the desorption occurs during the initial fall of the drops. In order to remove the sensitive drop size dependence on the desorption rate, Walcek et al. (1984) proposed the following relation:

$$T^* = \frac{D_L}{a_{32}^2} t \qquad (16)$$

The desorption time, T^*, is nondimensionalized with respect to the molecular diffusion time for each drop size category.

However, it appears that this time parameter is inadequate because the pure molecular diffusion does not control the mass transfer when the drops contain some form of internal circulation and oscillation. That is why (confirmed in Figure 9) the proposed model based on a local approach of interfacial transfer phenomenon through the interfacial friction velocity, which takes into account a part of the effect of turbulent mixing and oscillation inside large drops, seems to be more realistic than global models.

Discussion

We observe that whatever the type of absorption or desorption experiments, the present local model fits our experimental data very well. Moreover, we confirm the validity of a pseudo steady-state assumption, and it is interesting to underline that the value of the coefficient ω appearing in the proposed correlation is the same for all the cases, even if its determination is empirical. That is to say based on experiments with SO_2 and CO_2 which present a high contrast in solubility in water. Furthermore, this study confirms and generalizes the conclusion expressed earlier with regard to the comparison of the present model with literature data. In particular, as the value of the coefficient ω is always the same it can be considered as a constant.

Conclusion

A great amount of work has been devoted to the mass-transfer process to and from large water drops falling in the continuous phase, but failed to provide successful correlations for predicting the mass-transfer coefficient when resistance to penetration occurs in the liquid phase. The main conclusion of the present study emphasizes that our experimental results, as with those found in the literature review, are in full accordance with those predicted by a local model founded on the large eddy renewal concept of Fortescue and Pearson; this takes into account, as we have suggested, the drop diameter and the liquid interfacial friction velocity as characteristic length and velocity scales respectively. With regard to the ensuing conclusion, we highlight the capabilities offered by the 5-m rain shaft built and tested at the "Institut de Mécanique des Fluides de Toulouse." Reversible and irreversible absorption and desorption experiments of SO_2 from large drops that do not reach their terminal velocity have been performed which will give a good indication of the robustness of the model in a large spectrum of interfacial mass-transfer conditions. It is very interesting to note that the large eddy concept for gas-transfer prediction cover the case of absorption both in channel stratified turbulent flows and flows around large water drops, when models based on the small turbulent eddies (Lamont and Scott, 1970; Hasse et Liss, 1980; Coantic, 1986; Banerjee, 1990) cannot predict accurately the experimental results.

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Notation

a = equivalent drop radius
a_{32} = drop Sauter radius
c_{DF} = skin friction drag coefficient
c_{DP} = pressure drag coefficient
C_i = equilibrium concentration at the interface
$\langle C_i \rangle$ = average dissolved gas concentration in the liquid phase
d = equivalent drop diameter
Re = Reynolds number = Ud/ν_g
Re_* = interfacial Reynolds number in the liquid phase = $u_* d/\nu_L$
Re_s = local Reynolds number in the liquid phase = $U_s l_s/\nu_L$
Sc = Schmidt number in the liquid phase = ν_L/D_L
Sh = Sherwood number in the liquid phase = $K_L\ d/D_L$
t = dimensional contact time
T_* = dimensionless time = $D_L\ t/a_{32}^2$
u_* = interfacial liquid friction velocity

Greek letters

α = exponent
β = exponent
γ = exponent
κ = viscosity ratio = μ_L/μ_g
μ_g = dynamic viscosity of the gas
μ_L = dynamic viscosity of the liquid
ν_g = kinematic viscosity of the gas
ρ_g = gas density
ρ_L = liquid density
τ_s = interfacial shear stress
ω = coefficient

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Appendix: Equilibrium Hydrolysis Reactions of Sulfur Dioxide

Equilibrium relations for sulfur dioxide in water

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

$$SO_2 + H_2O \rightleftharpoons H_2SO_3 \qquad (A1)$$

$$H_2SO_3 + H_2O \rightleftharpoons H_3O^+ + HSO_3^- \qquad (A2)$$

$$HSO_3^- + H_2O \rightleftharpoons H_3O^+ + SO_3^= \qquad (A3)$$

The values of the equilibrium constants K_H, K_1 and K_2 of reactions A1, A2 and A3 are respectively:

$$K_H = \frac{[H_2SO_3]}{[SO_2]} = 7.1_* 10^{-4} \exp\left[\frac{3145}{T}\right] \text{ (moles/moles)} \qquad (A4)$$

$$K_1 = \frac{[HSO_3^-][H_3O^+]}{[H_2SO_3]} = 1.9_* 10^{-5} \exp\left[\frac{2022}{T}\right] \text{ (moles/liter)} \qquad (A5)$$

$$K_2 = \frac{[SO_3^=][H_3O^+]}{[HSO_3^-]} = 2.4_* 10^{-11} \exp\left[\frac{1671}{T}\right] \text{ (moles/liter)} \qquad (A6)$$

Where T is the absolute temperature expressed in Kelvin.

The total sulfur concentration [SIV] is written as:

$$[SIV] = [H_2SO_3] + [HSO_3^-] + [SO_3^=] \qquad (A7)$$

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

- Condition of electroneutrality:

$$[H_3O^+] = [OH^-] + [HSO_3^-] + 2[SO_3^=] \qquad (A8)$$

- Condition of water ionization:

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^- \qquad (A9)$$

- The equilibrium constant of the ionization of water is defined by:

$$K_W = [H_3O^+][OH^-] \text{ (that is, } K_W = 10^{-14} \text{ at } 25°\text{C)} \qquad (A10)$$

- The total sulfur concentration as a function of pH of the solution is given by:

$$[SIV] = \left([H_3O^+] - \frac{K_W}{[H_3O^+]}\right) \times \left(\frac{[H_3O^+]^2 + K_1[H_3O^+] + K_1K_2}{K_1[H_3O^+] + 2K_1K_2}\right) \qquad (A11)$$

For pH ≤ 5.5, reaction A3 may be neglected. Thus, the total S concentration is then given by:

$$[SIV] = [H_2SO_3] + [HSO_3^-] = \frac{[H_3O^+]^2 + K_1\,[H_3O^+]}{K_1} \qquad (A12)$$

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

$$[SIV]_{drop} = \left(\frac{V_{coll} + V_{drop}}{V_{drop}}\right) [SIV]_{coll} \qquad (A13)$$

From Eq. A12 and by measuring the pH = $-\log([H_3O^+])$ of this collected solution, we have:

$$[SIV]_{drop} = \left(\frac{V_{coll} + V_{drop}}{V_{drop}}\right) \frac{[H_3O^+]^2 + K_1\,[H_3O^+]}{K_1} \qquad (A14)$$

Equilibrium relations for sulfur dioxide in hydrogen peroxide

When sulfur dioxide is absorbed into the hydrogen peroxide solution, the sulfur S(IV) becomes converted to S(VI). The resulting equilibrium relation is written as:

$$HSO_4^- + H_2O \rightleftharpoons 2H_3O^+ + SO_4^= \qquad (A15)$$

The value of the equilibrium constant of this reaction is:

$$K_3\ (\text{moles l}^{-1}) = \frac{[SO_4^=][H_3O^+]}{[HSO_4^-]} = 0.012\ \text{mol/L} \qquad (A16)$$

After manipulations from this equation, together with the following considerations.

- Condition of electroneutrality:

$$[H_3O^+] = [HSO_4^-] + 2[SO_4^=] \qquad (A17)$$

- The total sulfur concentration, $[S^{VI}]$, is written as:

$$[S^{VI}] = [HSO_4^-] + [SO_4^=] \qquad (A18)$$

we find the concentration of S(VI) as a function of pH = $-\log([H_3O^+])$:

$$[S^{VI}] = \frac{[H_3O^+](K_3 + [H_3O^+])}{2K_3 + [H_3O^+]} \qquad (A19)$$

When the drops passed through the rain shaft, they were collected in a cup initially containing a volume of H_2O_2 noted V_{coll} in ml. If we designate, respectively, the total concentrations in the drop and in the collected solution as $[S^{VI}]_{coll}$ and $[S^{VI}]_{drop}$, and V_{drop} the drops volume in ml in the cup, we obtain from mass conservation of sulfur:

$$V_{drop}\,[S^{VI}]_{drop} = (V_{drop} + V_{coll})\,[S^{VI}]_{coll} \qquad (A20)$$

Since $[H_3O^+]$ is measured in the collector by pH measurements and NaOH titration, $[S^{VI}]_{coll}$ can be determined from Eq. A19. An expression for $[S^{VI}]_{drop}$ in terms of quantities measured in the experiment can be given by:

$$[S^{VI}]_{drop} = \left[\frac{V_{drop} + V_0}{V_{drop}}\right] \left[\frac{[H_3O^+]\,(K_3 + [H_3O^+])}{2K_3 + [H_3O^+]}\right] \qquad (A21)$$

Oxidation of sulfur (IV) by hydrogen peroxide

In order to calculate the rate of oxidation of S(IV) to S(VI) by hydrogen peroxide, we use the formulation given by Martin and Damschen (1981):

$$-\frac{\partial\langle[S^{IV}]\rangle}{\partial t} = \frac{\partial\langle[S^{VI}]\rangle}{\partial t} = \frac{8{*}10^{+4}\,[H_2O_2]\,[H_2SO_3]}{\{0.1 + [H_3O^+]\}} \qquad (A22)$$

For pH ≤ 5.5, the reaction A3 may be neglected and the condition for the neutrality A8 is given by: $[H_3O^+] = [HSO_3^-]$. Thus, we obtain the following relation:

$$-\frac{\partial\langle[S^{IV}]\rangle}{\partial t} = \frac{\partial\langle[S^{VI}]\rangle}{\partial t}$$
$$= \frac{8{*}10^{+4}\,[H_2O_2]\,[H_3O^+]}{\{0.1 + [H_3O^+]\} \bullet \{[H_3O^+] + K_1\}} \langle[S^{IV}]\rangle \qquad (A23)$$

From the equilibrium relations and the condition for electroneutrality we deduce the concentration of hydrogen ions as function of $[S^{IV}]$ and $[S^{VI}]$:

$$\begin{aligned}&[H_3O^+]^3 + \{K_1 + K_3 - \langle[S^{IV}]>\}\,[H_3O^+]^2 \\ &\quad + \{K_1K_3 - K_1\langle[S^{IV}]\rangle - (K_1 + 2\,K_3)\,\langle[S^{VI}]\rangle\}\,[H_3O^+] \\ &\quad - \{K_1K_3\langle[S^{IV}]\rangle + 2\langle[S^{VI}]\rangle\} = 0 \qquad (A24)\end{aligned}$$

Starting calculus from the expression of the flux at the interface, the concentration of hydrogen ions is determined from Eq. A24 and the conversion of S(IV) to S(VI) from Eq. A23. New concentrations are then obtained and the operation is repeated for the desired time. We assume that the concentration of hydrogen peroxide is uniform inside the drop.