

GAS TRANSFER FROM SMALL SPHERICAL BUBBLES IN NATURAL AND INDUSTRIAL SYSTEMS*

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ABSTRACT

The bubble terminal velocity and the mass transfer behavior of a small (diameter ≤ 0.2 cm) spherical bubble rising through stagnant water are reviewed. Equations relating the bubble diameter and gas composition as a function of depth are presented. The gas-liquid mass transfer co-efficient was estimated from observed bubble diameter versus time data reported in the literature. The system of equations has been solved by numerical integration to predict the behavior of a bubble as it rises through the water column. The model can predict the rate of dissolution and the change in composition of the bubble as a function of the depth of release, initial gas composition in the bubble, liquid phase gas composition, and gas temperature. The mass transfer correlation was found to compare favorably with the theoretical predictions. Initial bubble diameter and basin depths are the most significant parameters that control the gas transfer efficiency of the process. The results can assist in improving the design of experiments to evaluate the bubble terminal velocity and the mass transfer coefficient more accurately.

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INTRODUCTION

The exchange of gases between water and the atmosphere is a key process in nature and in a host of chemical and industrial operations. Release of bubbles under water is the most common method for enhancing gas transfer to water. A fundamental understanding of the gas transfer characteristics of bubbles is therefore essential for analyzing natural systems and designing efficient gas transfer devices and systems. Numerous researchers have conducted countless experiments to investigate the factors that influence the formation of gas bubbles and their gas transfer behavior. This article reviews the gas transfer behavior of small ascending bubbles, identifies some discrepancies in the reported results, presents a simple mathematical model to characterize the gas transfer behavior of bubbles under different conditions, and employs the model to characterize bubble behavior.

A bubble may be defined as a self-contained body of one gas or a mixture of gases, separated from its surrounding medium by recognizable interface [1]. A schematic diagram of a small spherical bubble rising through a stagnant water column is shown in Figure 1. As the bubble rises, water flows around the bubble. An examination of streamlines shows that there is considerable variation in the flow conditions around the bubble. Depending on the bubble size and terminal velocity, the formation and intensity of eddy currents will vary and, therefore, the thickness of liquid film will also vary dramatically across the bubble surface. As a result, the mass transfer coefficient will change from one part of the bubble surface to another. For application purposes, however, the variation is less important and the average mass transfer coefficient over the entire surface of the bubble is used for design and analysis of gas transfer systems. This article focuses on predicting the average mass transfer coefficient of bubbles.

The total external pressure on any bubble is the sum of atmospheric, hydrostatic, and surface tension pressure. When bubbles are formed or released under water, the partial pressures of gases within the bubbles are usually different from the equivalent liquid phase concentration of the same gas. As the bubbles rise, gas(es) may transfer between the bubble and the surrounding liquid as a result of concentration differences. The rate of gas transfer depends on bubble parameters such as diameter which affects both the surface area for mass transfer and the bubble terminal velocity, the partial pressure of gas(es) within the bubble, and the dissolved gas concentrations in the water. As gases enter or leave the ascending bubble, all these parameters change. Due to the complex nature of the system, mathematical modeling is the most effective tool to characterize the behavior of bubbles in water.

As a bubble rises through a stagnant water column, the dynamic behavior of the bubble water interface depends on the diameter of the bubble. For large bubbles, the interface moves freely and, therefore, the mass transfer coefficients of large bubbles are quite high. Small bubbles, on the other hand, retain their spherical

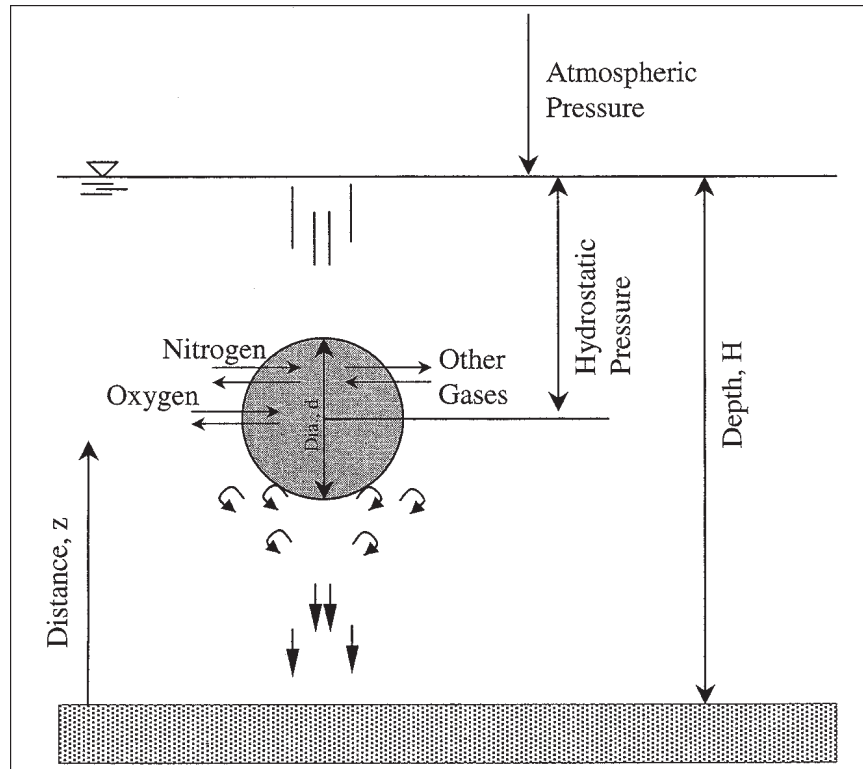


Figure 1. Gas transfer from a bubble rising through stagnant water.

shape and behave like solid particles [1] and as a result exhibit lower mass transfer coefficients. The exact diameter at which the transition from solid particle behavior to a freely moving interface is not clear. Coppock and Meiklejohn [2] measured gas transfer between air bubbles and gas free water and did not observe any significant difference in mass transfer coefficient for bubbles having diameters between 0.15 and 0.30 cm. Hammerton and Garner [3] investigated the rate of dissolution of individual gas bubbles rising in water and glycerol and found that the bubbles changed shape (commonly referred to as bubble circulation) freely at diameters greater than 0.02 cm. Motarjemi and Jameson [4] measured liquid phase mass transfer coefficient for oxygen bubbles rising in water and concluded that the surface of bubbles greater than 0.015 cm in diameter became mobile. However, Calderbank [5, 6] and Calderbank et al. [7] studied carbon dioxide absorption and demonstrated that bubble diameters greater than 0.22 cm were required to achieve bubble recirculation. The reasons for these discrepancies in the reported behavior of bubbles is not clear but may depend on a number of

factors such as the experimental setup, the gas, and the water quality studied. In this article, we assume that bubbles having diameters equal to or less than 0.22 cm behave as solid particles. This bubble size range is typical of the bubbles produced by fine bubble diffusers in wastewater treatment plant applications.

The dependence of bubble terminal velocity on bubble diameter has been studied by a number of investigators [4, 8, 9]. In addition to bubble diameter, the terminal velocity depends on the liquid properties and the presence of contaminants (e.g., surfactants, colloidal solids, etc.) in water [10]. Most bubble terminal velocity measurements were made by measuring the travel time of a single bubble rising in stagnant water between two reference depths. The investigators did not consider any diameter changes with time due to the exchange of gases. Therefore, there are some inherent errors associated with bubble terminal velocity measurement results. The magnitude of this error would be greater with greater distance between the two reference depths.

The terminal velocity as a function of bubble diameter is shown in Figure 2 [4]. For bubble diameter less than about 0.02 cm Stokes' Law can predict the terminal velocity. For diameters greater than 0.26 cm and less than 1.0 cm, the terminal velocity attains a constant value of approximately 24 cm/sec. The terminal velocities for intermediate diameter bubbles are also shown in the Figure 2. The three segments of the terminal velocity versus bubble diameter curve can be fitted with best-fit polynomials and used to estimate the bubble terminal velocity.

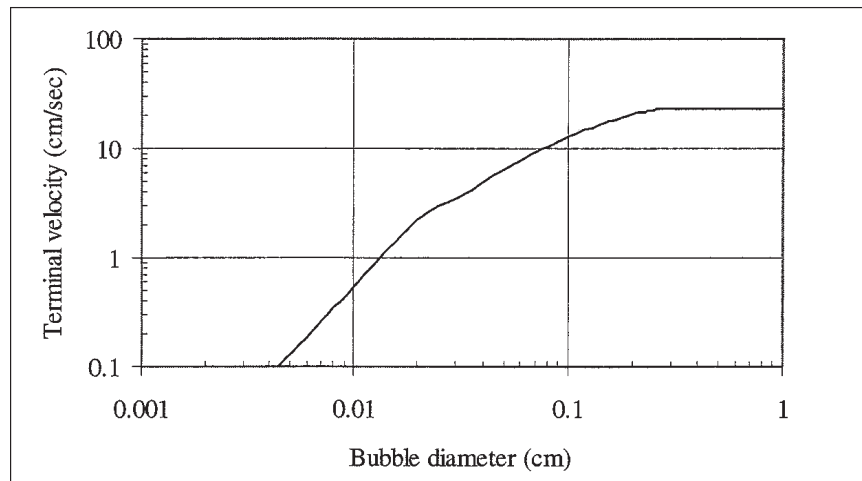


Figure 2. Measured terminal velocities of bubble in stagnant water from literature [4].

The gas transfer behavior of small bubbles has been studied extensively because of its importance in many chemical and industrial processes. A number of investigators [12-19] made empirical assumptions and used either the Karman integral method, the perturbation method or boundary layer theory to derive theoretical mass transfer correlations relating Sherwood number (Sh) with Reynolds (Re) and Schmidt (SC) number. These correlations were of the form:

$$\text{Sh} = a \text{Re}^b \text{Sc}^c$$

The values of the exponents b and c in all correlations are 0.5 and 0.33, respectively, with the exception of Friedlander [11], Frisch [12], and Kronig and Bruijsten [13]. The dimensionless correlations proposed by various investigators and their region of validity are given in Table 1. A number of investigators have published dimensionless correlations for estimating mass transfer coefficient using similar experimental systems. The experimental mass transfer correlations were based mainly on two types of test systems:

Experiments with Drops or Solid Spheres of Pure Compound

Frossling [14], Williams [20], Calderbank and Korchinski [21], and Griffith [22] studied the evaporation of pure volatile compounds to estimate the mass transfer characteristics of small bubbles. Although the experimental methods of these studies were not the same, the mass transfer coefficient values calculated

Table 1. Mass Transfer Correlation from Literature for Forced Convection from Small Spheres

Source	Region of Validity	Correlation
Frossling [14]	Not reported	$\text{Sh} = 0.6 \text{Re}^{0.5} \text{Sc}^{0.33}$
Williams [20]	$4 \leq \text{Re} \leq 400$	$\text{Sh} = 1.5 \text{Re}^{0.35} \text{Sc}^{0.33}$
Calderbank and Korchinski [21]	$1 \leq \text{Re} \leq 200$	$\text{Sh} = 0.43 \text{Re}^{0.56} \text{Sc}^{0.33}$
Barker and Treybal [23]	Not reported	$\text{Sh} = 0.02 \text{Re}^{0.833} \text{Sc}^{0.5}$
Griffith [22]	$\text{Re} > 1$	$\text{Sh} = 2 + 0.57 \text{Re}^{0.5} \text{Sc}^{0.35}$
Calderbank and Moo-Young [24]	Not reported	$k_L \text{Sc}^{2/3} = 0.31 \left(\frac{\Delta \rho \mu g}{\rho^2} \right)$
This Study	$0.01 \leq \text{Re} \leq 100$	$\text{Sh} = 0.4911 \text{Re}^{0.3824} \text{Sc}^{0.33}$

from the correlation are very similar as shown in Figure 3. The figure shows excellent agreement between various correlations.

Barker and Treybal [23] also presented (Table 1) a correlation to estimate the mass transfer coefficient from solid spherical particles suspended in agitated liquids. The calculated values are shown by the lower dotted line in Figure 3. The mass transfer coefficient values were lower than those obtained from the other correlations and the exponent of Reynolds and Schmidt number are 0.833 and 0.5, respectively.

Experiments with Bubbles

Calderbank and Moo-Young [24] obtained mass transfer correlation for small bubbles (diameter < 0.25 cm) using absorption of carbon dioxide gas into water containing various concentrations of glycerol. It should be emphasized that although the mass transfer coefficient was found to be independent of bubble terminal velocity, the actual values are very similar to the other studies as shown in Figure 3. The selection of carbon dioxide as the solute gas has been criticized because hydrolysis/reactions in the liquid phase may lead to higher mass transfer coefficients.

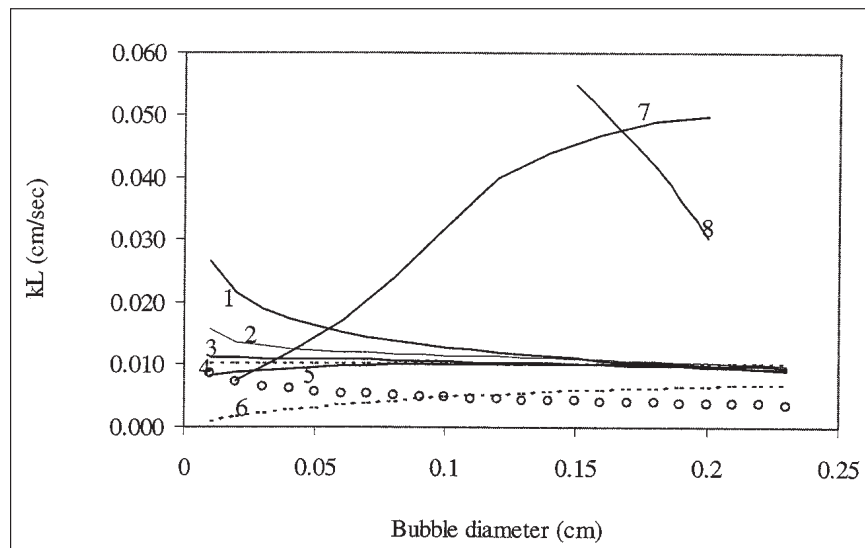


Figure 3. Comparison of observed values of mass transfer coefficients as a function of bubble diameter from literature. 1 – Williams, 2 – Griffith, 3 – Frossling, 4 – Calderbank and Moo-Young, 5 – Calderbank and Korchinski, 6 – Barker and Treybal, 7 – average line through Pasveer and Motarjemi and Jameson data points, and 8 – Coppock and Meiklejohn.

Several investigators used single air bubbles in an attempt to characterize the mass transfer behavior. The results are not all in agreement; there are significant differences in reported data. The discrepancies may be, in part, due to the variation in the experimental conditions employed. It is also possible that the design of the experimental apparatus did not effectively reproduce the fluid flow conditions required to simulate the simple rise of a bubble through a stagnant water column.

Motarjemi and Jameson [4] measured the mass transfer coefficients of small bubbles of diameter 0.01-0.1 cm, rising at terminal velocities in water. The mass transfer coefficients were found to be directly proportional to the diameter of the bubble and were much higher than those predicted by other investigators with the exception of Pasveer [25]. Pasveer found similar mass transfer coefficient values for air bubbles. An average line through all values from the two studies is shown in Figure 3. It was proposed that the bubble surfaces were to some extent mobile in contrast to the conventional "solid sphere" theory [25]. The effect of nitrogen in the transfer process was either neglected or not fully explained in these papers.

The mass transfer coefficient values reported by Coppock and Meiklejohn [2] are also shown in Figure 3. The air-water mass transfer coefficient values were found to decrease with increasing bubble diameter and vary from 0.028 to 0.055 cm/sec. However, they used gas free water in their studies and neglected the transfer of nitrogen and water vapor in their data analysis. Wyman et al. [26] and Detsch [27] also used air bubbles but these authors published much of their raw data, which we discuss below and use to check a simple bubble-gas-transfer model.

In summary, much of the published information on gas transfer from small bubbles is apparently contradictory. In light of the importance of this subject, it is somewhat surprising that these discrepancies remain unresolved.

THEORY

The gas transfer across the bubble water interface and the resulting change in gas composition and bubble size can be predicted using principles of diffusion. As shown in Figure 1, a spherical bubble is created and released at a depth H and it ascends through the water column. The bubble contains either a pure gas or a mixture of gases and is involved in the gas transfer process. Depending on the relative concentration of a component gas in the gas and liquid phases, the component may transfer from gas phase to liquid phase or vice versa. The concentration of any component in the bubble, however, varies with the volume of the bubble and the transfer of components to and from the surrounding liquid. As discussed earlier, the mass transfer coefficient and the terminal velocity of the bubble are functions of the diameter of the bubble and are known from literature. Focusing on oxygen transfer, the following assumptions simplify the model:

1. gas transfer across the bubble surface is the only process by which interfacial mass transfer takes place;
2. the initial bubble shape is spherical and it retains its original shape throughout its travel through the water column;
3. the bubble and the reservoir are completely mixed in the sense that they are each characterized by a single concentration of the component at any time;
4. the liquid reservoir is assumed to be large so that the component concentration in the liquid remains constant during the entire transfer process;
5. the effect of water vapor and dissolved gases other than nitrogen may be neglected; and
6. the mass transfer coefficient of oxygen and nitrogen are equal.

With these assumptions, the variables in the problem are: 1) number of moles of oxygen; 2) number of moles of nitrogen in the bubble; and 3) the size of the bubble as a function of distance of travel. The pressure in the bubble is also a function of bubble diameter and at a depth (H-z), is given by the following three components:

$$P = \left(\begin{array}{c} \text{atmospheric pressure} \\ \text{at the surface} \end{array} \right) + \left(\begin{array}{c} \text{hydrostatic} \\ \text{pressure} \end{array} \right) + \left(\begin{array}{c} \text{pressure due to} \\ \text{surface tension} \end{array} \right)$$

$$\text{Or, } P = P_s + \gamma (H - z) + \frac{2\sigma}{r} \quad (1)$$

where P_s = pressure at the surface, γ is the unit weight of water, H is the depth of the release point, z is the distance traveled by the bubble from the release point, σ is the surface tension of water, and r is the bubble radius. Differentiating and multiplying by the bubble volume V , yields:

$$V * \left(\frac{dP}{dz} \right) = - \left(\frac{4}{3} \pi r^3 \right) * \left[\gamma + \frac{2\sigma}{r^2} * \left(\frac{dr}{dz} \right) \right] \quad (2)$$

Referring to Figure 3, the mass balance of oxygen (in terms of moles) in the bubble leads to:

$$\left(\frac{dno}{dz} \right) = - \frac{4\pi r^2 k}{v} \left(\frac{no}{V * H_o} - co_w \right) \quad (3)$$

where no is the number of moles oxygen in the bubble at z , k is the mass transfer coefficient of oxygen, H_o is the Henry's Law constant for oxygen, co_w is the liquid phase oxygen concentration in the reservoir, V is the volume of the bubble, and v is the bubble terminal velocity at z . Similarly, the mass balance of nitrogen in the bubble is given by:

$$\left(\frac{dnn}{dz}\right) = -\frac{4\pi r^2 k}{v} \left(\frac{nn}{V^* H_N} - cn_w\right) \quad (4)$$

where nn is the number of moles of nitrogen in the bubble, H_N is the Henry's Law constant for nitrogen, cn_w is the liquid phase nitrogen concentration in the reservoir. Combining (3) and (4) and simplifying, we can write,

$$\left[\frac{d(no + nn)}{dz}\right] = \left[\frac{dn}{dz}\right] = -\frac{4\pi r^2 k}{v} \left(\frac{no}{V^* H_o} - co_w - cn_w + \frac{nn}{V^* H_N}\right) \quad (5)$$

From the gas law, $n = \frac{PV}{RT}$. Substituting the value of n in equation (5) yields:

$$\left[\frac{d(PV)}{dz}\right] = -\frac{4\pi r^2 kRT}{v} \left(\frac{no}{V^* H_o} - co_w - cn_w + \frac{nn}{V^* H_N}\right) \quad (6)$$

Now, differentiating the LHS of the above equation, substituting the value of $V(dP/dz)$ from Eq. (2) and simplifying yields:

$$\frac{d(PV)}{dz} = \left(\frac{dr}{dz}\right) \left(4\pi r^2 P - \frac{8}{3} \pi \sigma r\right) - \left(\frac{4}{3} \pi \gamma r^3\right)$$

Substituting and simplifying, eq. (6) becomes,

$$\left(\frac{dr}{dz}\right) = \frac{1}{M} \left[-\frac{4\pi r^2 kRT}{v} \left(\frac{no}{V^* H_o} - co_w - cn_w + \frac{nn}{V^* H_N}\right) + \left(\frac{4}{3} \pi \gamma r^3\right)\right] \quad (7)$$

where $M = \left(4\pi r^2 P - \frac{8}{3} \pi \sigma r\right)$. The (initial) boundary conditions for the above equation are:

at $z = 0$ (depth = H),

no = amount of oxygen in the bubble in moles,

nn = amount of nitrogen in the bubble in moles, and

r = initial radius of the bubble.

Equations (3), (4), and (7), subject to the above boundary conditions, can be solved using a Runge-Kutta routine to give gas composition and the radius of the bubble as a function of depth. The program requires an accurate initial gas content in the bubble and correlations that define the mass transfer coefficient (k) and the bubble terminal velocity (v) as a function of the bubble diameter. The model then calculates the gas composition in the bubble and the corresponding bubble radius as the bubble rises. In this way the program determines the gas transfer characteristics and behavior of the bubbles as a function of time and depth.

MASS TRANSFER COEFFICIENT ESTIMATION

A thorough review of relevant literature was conducted to obtain primary data on gas transfer behavior of small spherical bubbles. Although a large number of studies are reported in the literature, almost all of them present mass transfer coefficient data. Only two investigators [26, 27] were found to report the change in bubble diameter with time data.

Detsch [27] investigated the dissolution of 100 to 1000 μm diameter bubbles in reagent grade water, artificial seawater, and seawater between temperatures 6°C and 44°C . In the experiments, the bubbles were held at a constant water depth by a downward water flow. The downward water velocity of the water was the same as the terminal velocity of the bubbles. Gas transfer from the bubble to the surrounding water caused the bubbles to grow smaller with time. The test conditions simulated the free rise of bubbles through a water column except that the experimental apparatus maintained a constant hydrostatic pressure on the bubble throughout the duration of the test. The diameter of the bubble was photographed with time using a microscope and a motorized x-y manipulation table and the bubble diameter was measured using image analysis software. The effective resolution of analysis was $2\ \mu\text{m}$. The initial gas composition in the bubble and the physical parameters of the water was also reported. The observed bubble diameter versus time data are shown (as discrete points) in Figure 4. In order to

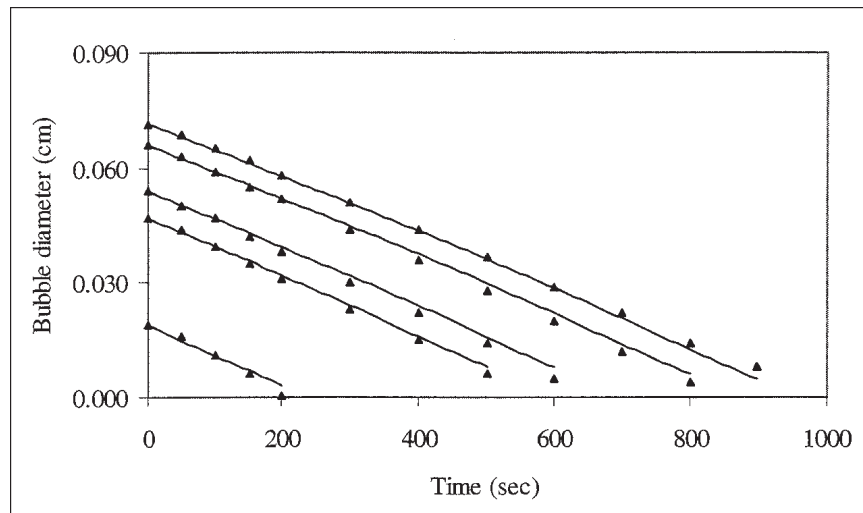


Figure 4. Calculated (using the model) and observed (Detsch data) bubble diameter as a function of time in seawater.

interpolate the intermediate diameter values, least square straight lines were fitted through the observed points (not shown). In all cases the R^2 value was 0.999.

Data Analysis: Equation (5) in terms of t can be written as:

$$\frac{dn}{dt} = -4\pi r^2 k \left(\frac{no}{V^* H_o} - co_w - cn_w + \frac{nn}{V^* H_N} \right) \quad (8)$$

$$\text{or, } \int_{n_o}^{n_t} dn = -k \int_0^t 4\pi r^2 \left(\frac{no}{V^* H_o} - co_w - cn_w + \frac{nn}{V^* H_N} \right) dt \quad (9)$$

Since the bubble diameter versus time data were available, the left-hand side of the equation can be evaluated using the gas law as:

$$n_t - n_{t+\Delta t} = \frac{P^* \Delta V}{RT} \quad (10)$$

The quantity under the integral of right hand side of the equation can be evaluated using initial gas and liquid phase concentrations. Therefore, the instantaneous mass transfer coefficient as a function of bubble diameter can be determined using the equation. The bubble terminal velocity corresponding to bubble diameter was estimated from Figure 2.

In order to normalize the experimental data and to examine the dependence of mass transfer coefficient on various factors, mass transfer data are conveniently expressed in terms of dimensionless Sherwood (Sh), Reynolds (Re), and Schmidt (Sc) numbers. The bubble diameter versus time data were not available at various temperatures and molecular diffusivities, therefore, a 1/3 power Schmidt number dependence was assumed from literature [14]. Figure 5 plots the experimental data as Sherwood number versus the Reynolds number. A least-square regression analysis of the data gave:

$$Sh = 3.7609 Re^{0.3824}$$

$$\text{Or, } Sh = 0.4911 Re^{0.3824} Sc^{0.33} \quad (0.01 > Re > 100) \quad (11)$$

The data in the Figure 5 show an excellent fit with very little scatter ($R^2 = 0.989$). The limitation of the correlation is that it is based on the experimental data for seawater reported by Detsch [27] only. In addition, tap water bubble terminal velocity were (Figure 2) used to estimate the terminal velocity of bubbles for seawater. Nonetheless, the above correlation compares favorably with earlier correlation in the literature as listed in Table 1. The mass transfer coefficients as a function of bubble diameter were also calculated and plotted in Figure 3 (as open circles).

The model equations (3), (4), and (7) developed in the previous section can be modified to represent the Detsch [27] experimental conditions (see Appendix A). The final equations in terms of time, t rather than the distance z are as follows:

$$\left(\frac{dno}{dt}\right) = -4\pi r^2 k \left(\frac{no}{V^* H_o} - co_w \right) \quad (12)$$

$$\left(\frac{dnn}{dt}\right) = -4\pi r^2 k \left(\frac{nn}{V^* H_N} - cn_w \right) \quad (13)$$

$$\left(\frac{dr}{dt}\right) = \frac{1}{M} \left[-4\pi r^2 kRT \left(\frac{no}{V^* H_o} - co_w - cn_w + \frac{nn}{V^* H_N} \right) \right] \quad (14)$$

where $M = \left(4\pi r^2 P - \frac{8}{3} \pi \sigma r \right)$. The (initial) boundary conditions for the above equation are:

- at $t = 0$ (depth = H = constant),
- no = amount of oxygen in the bubble in moles,
- nn = amount of nitrogen in the bubble in moles, and
- r = initial radius of the bubble.

As discussed in the previous section, the equations were solved numerically to give bubble diameter as a function of time as shown by solid lines in Figure 4. Although the mass transfer coefficients were extracted using the same data, the figure shows very good fit with little scatter.

Wyman et al. [26] conducted laboratory experiments to determine the rate of solution and change of composition of air bubbles in stirred seawater as a function

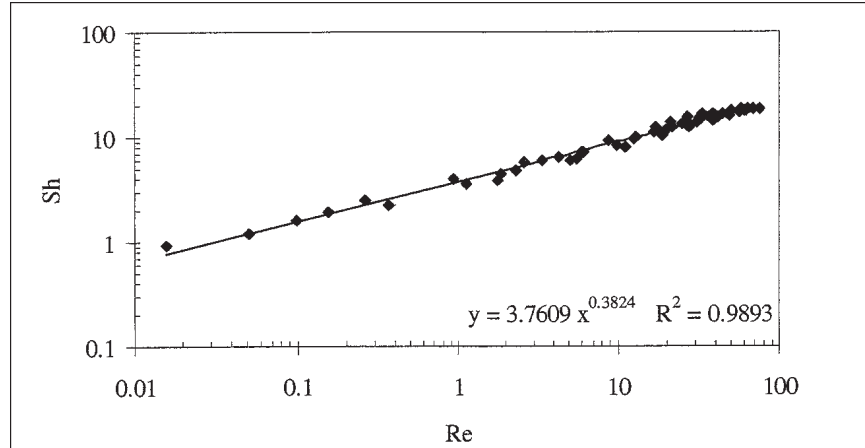


Figure 5. Sherwood number as function of the Reynolds number for small bubbles in seawater (Detsch data).

of depth. The apparatus consisted of glass bulbs with two ports; one for introducing air bubbles and the other for controlling the pressure using a mercury tube and a reservoir. The bulbs could be pressurized corresponding to those at depths of 5 to 200 m. The seawater used was filtered and equilibrated with air at the desired water bath temperatures (1 to 27°C). During a test, an air bubble was held at the center of the bulb by rotating the bulb by a drive. The change of bubble diameter with time was measured through a glass window using an ocular micrometer. Due to the rotation of the glass bulb, the direction of flow of water was in the tangential direction. The initial diameter of bubbles was about 0.5 cm which was much larger than the small bubble limit (i.e., ~ 0.2 cm). Therefore, the data were not analyzed and combined with Detsch [27] data. The bubble diameter versus time plot clearly showed that the rate of reduction of bubble diameter decreased with time. This may be due to the higher mass transfer coefficient values of large bubbles in comparison to small bubbles.

RESULTS AND DISCUSSION

Mass Transfer Behavior of Small Bubbles

The gas transfer model was employed to examine the mass transfer behavior of small bubbles rising in a large volume of stagnant water such that the external dissolved gas concentrations remained constant. Unless otherwise stated, the temperature for the following cases was set at 20°C.

Oxygen and Air Bubbles Rising through Deoxygenated Water

This first case examines the behavior of 0.1 cm bubbles of either air or pure oxygen rising from a release depth of 5 m. The water is assumed to be deoxygenated so that the external dissolved oxygen is zero and the dissolved nitrogen is in equilibrium with the atmospheric nitrogen partial pressure of 0.87 kPa (0.79 atm). The bubble diameter and release depth represent values typical in wastewater treatment plant aeration tanks although, as noted above, we do not take into account bubble-bubble interactions or changes in dissolved gas concentration in our analysis.

The calculated change in bubble diameter as a function of depth is shown in Figure 6. The “no transfer” case is presented to show how the bubble diameter changes as the bubble rise through the water if no gas transfer is allowed. In this case the bubble expands as a result of reduced surface tension and hydrostatic pressure and the diameter increases as shown. With gas transfer, the diameter of bubbles still increases with decreasing depth but to a lesser degree. It is also apparent that the diameter of the air bubble appears to increase more than that of the oxygen bubble.

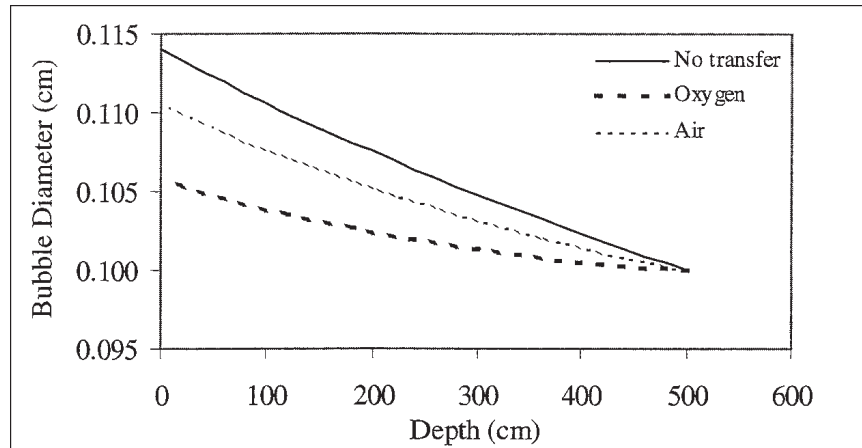


Figure 6. Oxygen and air bubble diameter as a function of depth.

The differences in bubble behavior between the air and pure oxygen bubble can be explained by examining the changes in gas content as the bubbles rise through the water. The variation of gas content of the oxygen and the air bubbles as a function of depth is shown in Figures 7a and 7b, respectively. For both bubbles, oxygen transfer from the bubble to the surrounding liquid causes the oxygen content to decrease as the bubbles rise. In the case of pure oxygen, the oxygen partial pressure is approximately 5 times higher and, therefore, oxygen transfer rate is also approximately 5 times faster. Another significant difference in behavior between the bubbles arises from differences in nitrogen gas transfer. For an oxygen bubble, there is a significant backdiffusion of nitrogen from the liquid to the bubble, with a corresponding increase in nitrogen content as the bubble rises as shown in Figure 7a. By comparison, for an air bubble, the nitrogen content of the bubble actually decreases slightly as shown in Figure 7b. The hydrostatic pressure on the bubbles is responsible for this reduction in nitrogen content. When the air bubble is released at a depth of 5.0 m, the pressure inside the air bubble is 50 percent higher than the atmospheric pressure and this encourages nitrogen to transfer from the air bubble to the water.

In the aeration industry, the oxygen transfer efficiency (OTE) is a measure of the performance of aeration systems. OTE is defined as the percentage of the oxygen originally in the bubble that is transferred to the water by the time the bubble reaches the surface. Interestingly, although pure oxygen bubbles transferred more oxygen, when the OTEs of air and oxygen bubbles are compared the two gases behave almost identically, as shown for different initial bubble diameters in Figure 8. With an initial bubble diameter of 0.03 cm 100 percent OTE

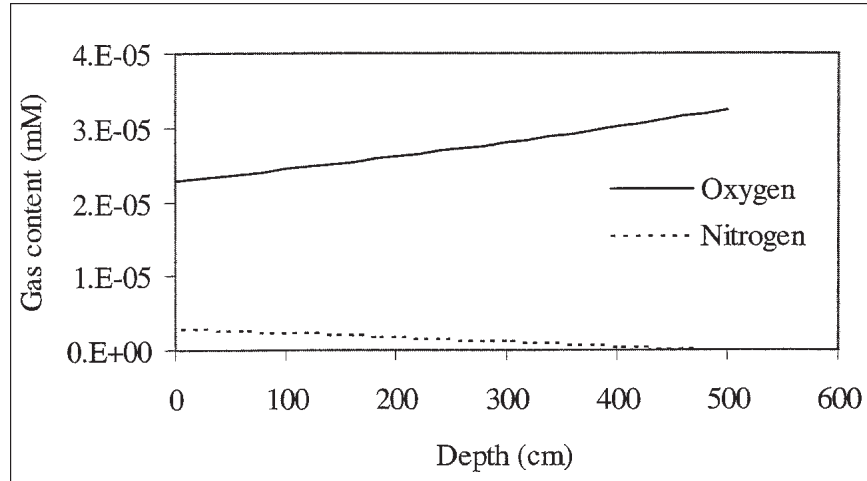


Figure 7a. Changes in bubble gas composition arising from gas transfer in an ascending oxygen bubble released at a depth of 5 m in deoxygenated water.

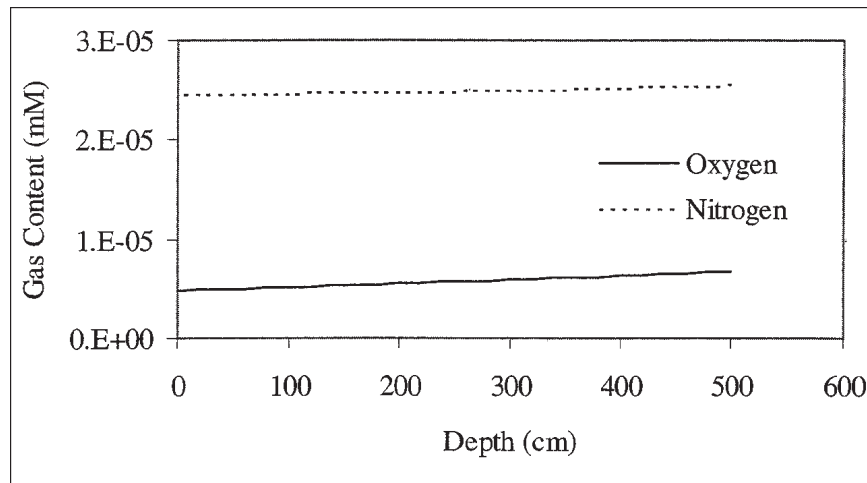


Figure 7b. Changes in bubble gas composition arising from gas transfer in an ascending air bubble released at a depth of 5 m in deoxygenated water.

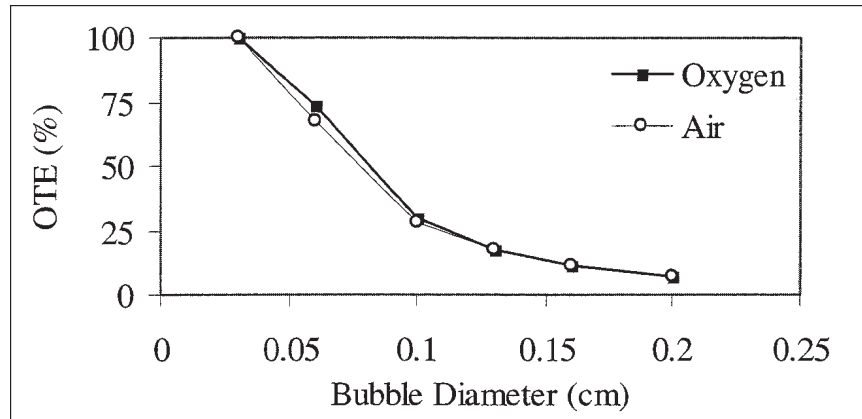


Figure 8. Calculated oxygen transfer efficiency as a function of bubble diameter for oxygen and air bubbles released at a depth of 5 m in deoxygenated water.

was achieved for bubbles released at a depth of 5.0 m. It was apparent, however, that the OTE dropped quickly as the bubble diameter increased. Additional predictions of OTE for different release depths indicated almost identical behavior of air and gas bubbles below 5.0 m as shown in Figure 9.

Figure 10 examines the behavior of a 0.06 cm diameter pure oxygen bubble rising from a depth of 15.0 m that achieves a 100 percent oxygen transfer efficiency. As mentioned earlier, the dissolved oxygen concentration of water is assumed to be zero and the dissolved nitrogen is in equilibrium with the atmospheric nitrogen. The bubble completely dissolves in water. The calculated numbers near the surface become extremely small and unreliable and therefore are not shown in the plot. The relative gas content (in percent) of the bubble as a function of depth is shown in Figure 11. The oxygen content declines with decreasing depth with a simultaneous increase in nitrogen content. As all the oxygen is transferred into the surrounding liquid the bubble contains nitrogen only, as indicated in the Figure. Figure 12 shows that the oxygen flux is from the bubble to the liquid and decreases gradually along the depth. The flow of nitrogen is from liquid to the bubble initially. However, due to the loss of oxygen the bubble becomes nitrogen rich and the partial pressure of nitrogen exceeds the equilibrium atmospheric nitrogen pressure at a depth of about 9.50 m. At this point, the nitrogen flux reverses its direction. The gas phase oxygen and nitrogen concentration in the bubble is shown in Figure 13. The horizontal line in the figure represents gas phase nitrogen concentration in the surrounding water. Again, it shows that the nitrogen concentration in the bubble exceeds the equilibrium concentration at a depth of about 9.50 m.

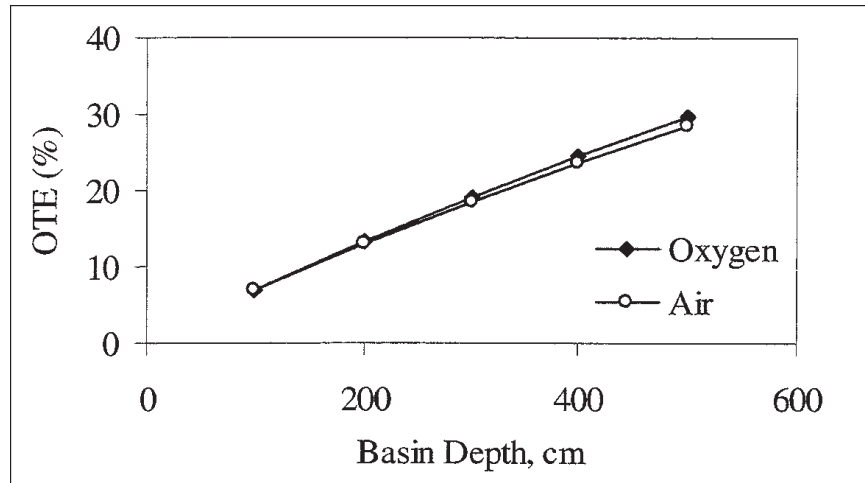


Figure 9. Calculated oxygen transfer efficiency as a function of basin depth for oxygen and air bubbles (diameter = 0.1 cm) in deoxygenated water.

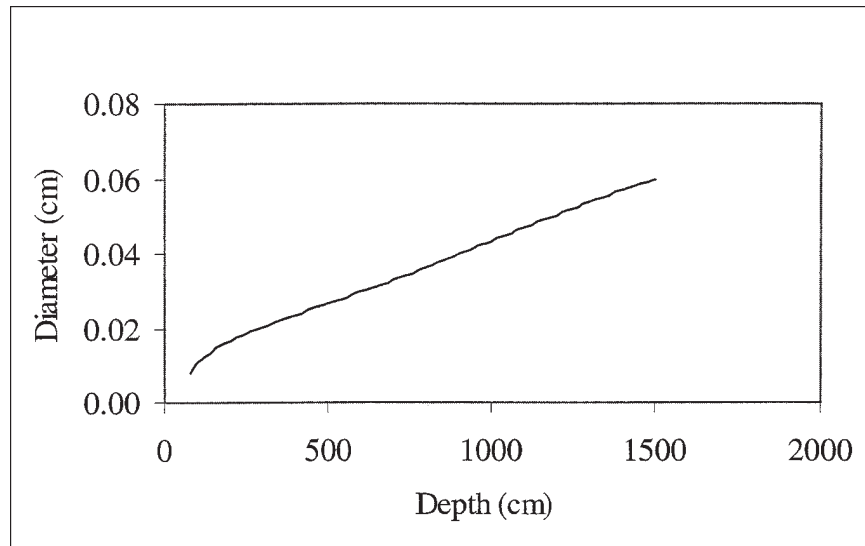


Figure 10. Calculated diameter of an ascending air bubble released at a depth of 15 m in deoxygenated water.

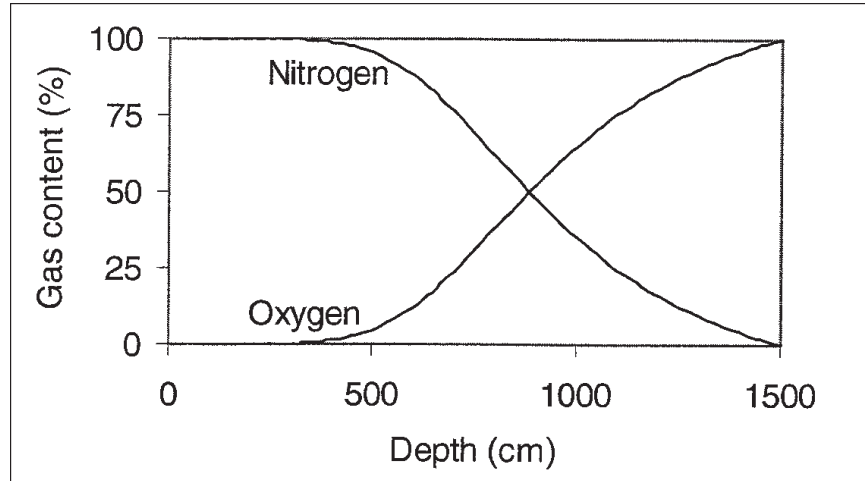


Figure 11. Change in bubble gas composition arising from gas transfer in an ascending oxygen bubble released at a depth of 15 m in deoxygenated water.

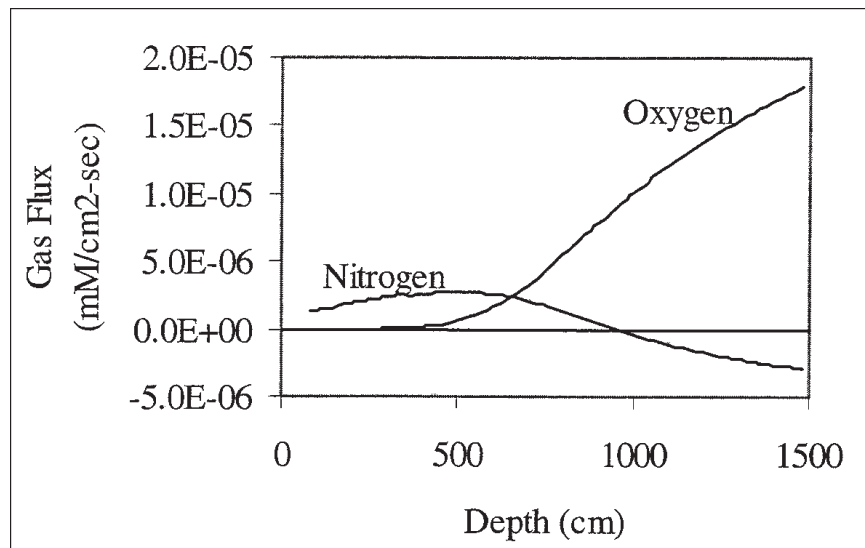


Figure 12. Change in gas flux arising from gas transfer in an ascending oxygen bubble released at a depth of 15 m in deoxygenated water.

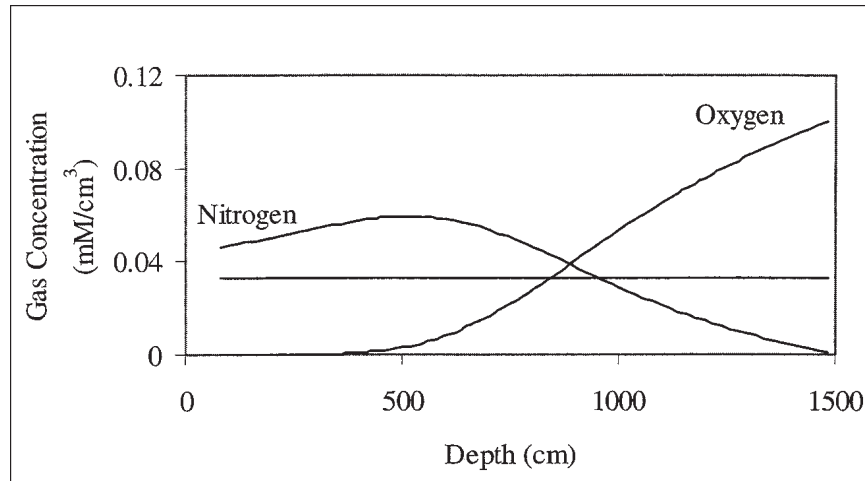


Figure 13. Change in gas concentration arising from gas transfer in an ascending oxygen bubble released at a depth of 15 m in deoxygenated water.

CONCLUSIONS

The article presents a mathematical model for simulating the mass transfer behavior of small single spherical bubbles (diameter ≤ 0.2 cm) as they rise through stagnant water column. The bubbles are assumed to retain their spherical shape and there is no bubble-bubble interaction. The model also incorporated effect of physical properties of the gas(es) in the bubble and the liquid medium (such as temperature, surface tension, liquid phase gas concentrations etc.). The following dimensionless correlation has been proposed to estimate the gas transfer coefficient for small spherical bubbles in stagnant seawater:

$$Sh = 0.4911 Re^{0.3824} Sc^{0.33} \quad (0.01 \geq Re \geq 100)$$

The model characterizes the behavior of small bubbles in seawater, under idealized conditions. It should be noted that the model, in its current form, might not be applicable to actual bubble aeration systems. However, with the availability of the model, experiments may be designed and conducted to estimate the bubble terminal velocity and mass transfer coefficient as a function of bubble diameter more accurately. The effect of various factors affecting the mass transfer coefficient and the terminal velocity of small bubbles also needs further investigation.

NOMENCLATURE

c_{o_w}	=	bulk liquid phase oxygen concentration (M/L ³)
c_{n_w}	=	bulk liquid phase nitrogen concentration (M/L ³)
d	=	diameter of the bubble (L)
D	=	molecular diffusivity of gas in water (L ² /T)
H	=	total depth of release (L)
H_o	=	dimensionless Henry's law coefficient for oxygen
H_N	=	dimensionless Henry's law coefficient for nitrogen
k	=	mass transfer coefficient across bubble water interface (L/T)
n	=	sum of moles of oxygen and nitrogen in the bubble (M)
n_o	=	number of moles of oxygen in the bubble (M)
n_n	=	number of moles of nitrogen in the bubble (M)
n_t	=	sum of moles of nitrogen and oxygen at time t (M)
$n_{t+\Delta t}$	=	sum of moles of nitrogen and oxygen at time $(t+\Delta t)$ (M)
P	=	total pressure on the bubble (M/LT ²)
P_s	=	atmospheric pressure in the system (M/LT ²)
R	=	universal gas constant (L ² /°KT ²)
r	=	radius of the bubble (L)
T	=	absolute temperature of the system, °K
V	=	volume of spherical bubble (L ³)
v	=	terminal velocity of bubble through stagnant water column (L/T)
z	=	distance traveled by the bubble from the point of release (L)
γ	=	unit weight of water (M/L ² T ²)
σ	=	surface tension of water (M/T ²)
ρ	=	density of water (M/L ³)
ν	=	kinematic viscosity of water (L ² /T)

Dimensionless Numbers

Sh	=	Sherwood Number = $\frac{kd}{D}$
Re	=	Reynolds Number = $\frac{vd}{\nu}$
Sc	=	Schmidt Number = $\frac{\nu}{D}$

APPENDIX A

Since the depth was kept constant in the experiments [27], the pressure may be represented as:

$$P = P_s + \gamma(H-z) + \frac{2\sigma}{r}$$

$$\text{Or, } P = P_s + \gamma H + \frac{2\sigma}{r}$$

Differentiating,

$$\frac{dP}{dt} = -\frac{2\sigma}{r^2} \frac{dr}{dt} \quad (\text{A1})$$

Since $z = vt$, Eqs. (3) and (4) may be written as:

$$\left(\frac{dno}{dt} \right) = -4\pi r^2 k \left(\frac{no}{V^* H_o} - co_w \right) \quad (\text{A2})$$

$$\left(\frac{dnn}{dt} \right) = -4\pi r^2 k \left(\frac{nn}{V^* H_N} - cn_w \right) \quad (\text{A3})$$

Adding Eqs. (A2) and (A3), we get,

$$\left[\frac{d(no + nn)}{dt} \right] = \left[\frac{dn}{dt} \right] = -4\pi r^2 k \left(\frac{no}{V^* H_o} - co_w - cn_w + \frac{nn}{V^* H_N} \right)$$

Since $PV = nRT$, the above equation reduces to:

$$\left[\frac{dPV}{dt} \right] = -4\pi r^2 k RT \left(\frac{no}{V^* H_o} - co_w - cn_w + \frac{nn}{V^* H_N} \right) \quad (\text{A4})$$

Differentiating the LHS of the above equation, substituting for (dP/dt) and simplifying yields,

$$\begin{aligned} \left[\frac{dPV}{dt} \right] &= V \left[\frac{dP}{dt} \right] + P \left[\frac{dV}{dt} \right] \\ &= \left(\frac{4}{3} \pi r^3 \right) \left(-\frac{2\sigma}{r^2} \frac{dr}{dt} \right) + 4\pi r^2 P \left(\frac{dr}{dt} \right) \\ &= \left(\frac{dr}{dt} \right) \left(4\pi r^2 P - \frac{8}{3} \pi \sigma r \right) \end{aligned} \quad (\text{A5})$$

Using Eq. (A5), Eq. (A4) reduces to:

$$\left(\frac{dr}{dt} \right) = \frac{1}{M} (-4\pi r^2 k RT) \left(\frac{no}{V^* H_o} - co_w - cn_w + \frac{nn}{V^* H_N} \right) \quad (\text{A6})$$

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