A numerical modelling of gas exchange mechanisms between air and turbulent water with an aquarium chemical reaction

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ABSTRACT

This paper proposes a new numerical modelling to examine environmental chemodynamics of a gaseous material exchanged between the air and turbulent water phases across a gas–liquid interface, followed by an aquarium chemical reaction. This study uses an extended concept of a two-compartment model, and assumes two physicochemical substeps to approximate the gas exchange processes. The first substep is the gas–liquid equilibrium between the air and water phases, \( A(g) \rightleftharpoons A(aq) \), with Henry's law constant \( H \). The second is a first-order irreversible chemical reaction in turbulent water, \( A(aq) + H_2O \rightarrow B(aq) + H^+ \) with a chemical reaction rate \( \kappa_A \). A direct numerical simulation (DNS) technique has been employed to obtain details of the gas exchange mechanisms and the chemical reaction in the water compartment, while zero velocity and uniform concentration of \( A \) is considered in the air compartment. The study uses the different Schmidt numbers between 1 and 8, and six nondimensional chemical reaction rates between \( 10^{-\infty} (\approx 0) \) to \( 10^1 \) at a fixed Reynolds number. It focuses on the effects of the Schmidt number and the chemical reaction rate on fundamental mechanisms of the gas exchange processes across the interface.

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0. Significance and novelty of this article

- This article provides a new concept and modelling strategy for a gas exchange process at a gas–liquid interface, followed by an aquarium chemical reaction. This article considers the gas exchange processes across the interface by separating this phenomenon into two physicochemical substeps; the first is a gas–liquid equilibrium of the gas at the interface, and second an aquarium chemical reaction. The modelling strategy is useful to evaluate the gas exchange rate of a highly reactive gas in water, with a lot of applicabilities in the fields of environmental sciences, atmospheric physics, chemical and mechanical engineering, and limnology.
- This article examines the effects of the Schmidt number of the gas, and the chemical reaction rate, on the gas exchange rate at the interface. The numerical data and results provided in this article are new and comprehensive, and show significant role of the chemical reaction in water on the gas exchange at the interface.

1. Introduction

Chemodynamics of a gaseous material exchanged between the air and turbulent water phases is one of the commonly observed physicochemical processes in the environment. One of the most well-known examples of the gas exchange is an...
uptake of carbon dioxide (CO$_2$) from the atmosphere into the ocean, and vice versa, across the ocean surfaces [1–4]. The gas exchange has been considered as one of the important processes of the global carbon cycle, and many field measurements of the gas exchange rate have been attempted to quantify the role of the ocean storage of CO$_2$ on the global budgets of carbon [5]. The gas exchange mechanisms between the atmosphere and river water have also been under scrutiny to clarify microbiological mass balances of CO$_2$ and oxygen (O$_2$) in the field of limnology [6,7].

Several reports have expressed concerns that CO$_2$ uptaken across the interface causes acidification of the seawater, since it is believed to have potential environmental and ecological impacts [8]. A series of chemical reactions of CO$_2$ in the seawater are expressed as [9],

\[
\begin{align*}
\text{CO}_2(g) & \rightleftharpoons \text{CO}_2(aq) \\
\text{CO}_2(aq) + \text{H}_2\text{O} & \rightleftharpoons \text{H}_2\text{CO}_3 \\
\text{H}_2\text{CO}_3 & \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \\
\text{HCO}_3^- & \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}
\end{align*}
\]

(1a–1d)

The first substep indicates the gas–liquid equilibrium of CO$_2$ between the two phases, and the following three substeps are the chemical reactions of CO$_2$ into the seawater. The effect of the chemical reaction rates of CO$_2$ in the seawater on the gas exchange rate should be investigated carefully to clarify details and future development of the ocean acidification, and to assess possible impacts on the ecosystem in the ocean, as well as the details of the global carbon cycle.

Another example of the environmental chemodynamics of a gas exchanged between air and water with the chemical reaction is production of trifluoroacetic acid, CF$_3$COOH, which is known as TFA [10,11]. This substance is one of the degradation products of 1,1,1,2-tetrafluoroethane (CH$_2$FCF$_3$), or, HFC-134a, which has been used as a refrigerant of a mobile fleet [12]. A few studies on the atmospheric chemistry have pointed out that HFC-134a is broken down by a series of stratospheric photochemical reactions after it is emitted into the atmosphere [13,14], and trifluoroacetyl fluoride, CF$_3$COF, is one of the degradation products of the photochemical reactions [10,11]. CF$_3$COF is further broken down to TFA by hydrolysis in cloud moistures following the physicochemical processes with the aid of ultraviolet rays [13,14],

\[
\begin{align*}
\text{CF}_3\text{COF}(g) & \rightleftharpoons \text{CF}_3\text{COF}(aq) \\
\text{CF}_3\text{COF}(aq) + \text{H}_2\text{O} & \rightarrow \text{CF}_3\text{COOH} + \text{HF}
\end{align*}
\]

(2a–2b)

TFA is one of the materials having strong organic acidity, and can accumulate in a closed surface water such as a seasonal wetland after wet depositions because of its low decomposition potential in the environment [15]. Both modelling of the formation processes of TFA, and predictions of its concentration in rainwater are desired to assess the details of accumulation in closed surface waters, and the biochemical effect of TFA on aquarium ecosystem [16].

Physicochemical processes of formation of the acid rain in cloud droplets caused by, for example, sulphur dioxide (SO$_2$) released into the atmosphere also involve hydrolysis shown by [17]

\[
\begin{align*}
\text{SO}_2(g) + \text{H}_2\text{O} & \rightleftharpoons \text{SO}_2 \cdot \text{H}_2\text{O} \\
\text{SO}_2 \cdot \text{H}_2\text{O} & \rightleftharpoons \text{H}^+ + \text{HSO}_4^- \\
\text{HSO}_4^- & \rightleftharpoons \text{H}^+ + \text{SO}_4^{2-}
\end{align*}
\]

(3a–3c)

The physicochemical processes explained above suggest that the gas exchange between air and water with an aquarium chemical reaction play an important role in determining chemodynamics of the gaseous substances in the environment.

Quantification of the gas exchange processes between air and water has been examined extensively in the fields of oceanography, and environmental sciences for the reasons expressed above. References which discuss the effect of the chemical reaction on gas transport processes into turbulent water are, however, extremely sparse. For example, many field measurements of the gas exchange rates at the atmosphere–ocean interfaces have been reported without considering the chemical reactions of CO$_2$ [18,19]. Also, many numerical studies on the gas exchange processes based on a direct numerical simulation (DNS) [20–24], and a large-eddy simulation technique (LES) [25–27], have not considered the effect of the aquarium chemical reactions. One of the reasons for the sparsity of references is that field and laboratory measurements on the gas exchange mechanisms with the aquarium chemical reactions are difficult, especially if the chemical reactions are fast. One of the good examples of the difficulties of measuring chemical reaction processes of the gases across the interface are indicated in a report by De Bruyn et al. [28], in which both Henry’s law constants and the chemical reaction rates for several halides are obtained by several studies. Table 1 in their report [28] suggests that very large uncertainties exist in the measurements of Henry’s law constant, and the chemical reaction rates of halides, resulting in considerable errors of predictions of the gas exchange rates. Another reason for the neglected effect of the aquarium chemical reactions on the gas exchange processes is that many researchers and scientist have not been aware of the critical roles of the aquarium chemical reactions on the gas exchange between air and water.

It should also be pointed out here that field and laboratory measurements of the gas exchange processes require observations of very fine-scale concentration and velocity fluctuations particularly in the near-interface turbulent boundary.
layer, because of a large Schmidt number of $O(10^3)$. The current hardware of a high-performance computing system, on the other hand, will not allow us to perform DNS of turbulent flows with the gas exchange of such a large Schmidt number. While LES methodology is available to compute the gas exchange at the interface for $Sc \sim O(10^2)$ [25–27], accuracy and reliability of the numerical solutions depend strongly on the subgrid-scale eddy diffusivity. It seems to be recognized under the present circumstances that the subgrid-scale eddy diffusivity modelling of large Schmidt number gas exchange problems need more sophistication, especially in the case of large Reynolds number turbulence. Introducing the effect of the chemical reactions in water on the gas exchange processes may require additional efforts to modify the eddy diffusivity modelling of the reactive gases. We need careful examination to model the gas exchange processes at the interface with the aquatic chemical reactions in more comprehensive manner.

This study proposes a new framework of a numerical modelling of the gas exchange between air and water across their interface, and subsequent chemical reaction in water based on an extended two-compartment model. The major purpose of this study is to provide a fundamental concept for modelling physicochemical processes of the gas exchange, followed by the chemical reaction in water. Demonstrating fundamental data and knowledge on the important environmental transport phenomena, especially the effects of the Schmidt number and the chemical reaction rate on the gas exchange mechanisms across the interface have also been attempted. The gas exchange processes are separated into two physicochemical substeps, the first is the gas–liquid equilibrium between the two phases, and the second is the chemical reaction in the water phase. A first-order, irreversible chemical reaction of the gaseous material after its uptake into the water phase is assumed here to simplify interactions of the chemical reactions and turbulent transport phenomena in water. While a traditional two-compartment model assumes uniform concentration of a material in each compartment, the present two-compartment model uses a computational fluid dynamics (CFD) technique in the water compartment to evaluate temporal development of three-dimensional profiles of the velocity and concentration fields. A direct numerical simulation (DNS) approach is used to evaluate profiles of fluid velocities and concentrations in water, and several important turbulence statistics have been evaluated without using turbulent closures, and subgrid-scale models. We assume that a fluid flow in the water phase is a well-developed turbulent water layer of a low Reynolds number, and the Schmidt number is varied from 1 to 8 to observe the effects of the molecular diffusion of the gas in sub-interface water on the gas exchange rate at the interface. Six degrees of the nondimensional chemical reaction rate are used to find the effect of the chemical reaction rate on the gas exchange mechanisms. Extrapolations of the gas exchange rates and the related transport phenomena toward larger Schmidt number and the faster chemical reaction rate will also be examined to predict the gas exchange processes of the actual gases of $Sc \sim O(10^2)$ based on results from the present numerical experiments.

2. Modelling of gas exchange processes between air and water

2.1. An extended two-compartment model

This study introduces an extended version of a two-compartment concept to model the environmental gas exchange processes between the air and water phases. Fig. 1(a) shows a schematic representation of the two compartments for considering the gas exchange between the air and water phases. The compartment of the air phase is filled with the gas A with a constant concentration $C_A^G$ and temperature $T$, and the law of the ideal gas is satisfied in it. The partial pressure of A in the compartment is expressed by $p_A = C_A^G R T$, using the gas constant $R$. The gas in the compartment does not have any flow velocities, and they are assumed zero everywhere in it. Fig. 1(b) demonstrates outlook of the structure in the compartment of the water phase. While a traditional two-compartment model assumes uniform concentration of a material in each compartment, this study considers three-dimensional unsteady distributions of the fluid velocity and concentrations only in the water compartment. We assume that a well-developed turbulent water layer bounded by a solid bottom and a flat gas–liquid interface is established in the compartment [20,22,24]. Sizes of the compartment are $L_x$ in length, $L_y$ in width, and $\delta$ in height, and the two boundaries of the compartment at $z=0$ and $\delta$ correspond to a gas–liquid interface, and a solid bottom, respectively.

This study separates the gas exchange processes into the two physicochemical substeps. The separation of the physicochemical processes is illustrated in Fig. 1(a) schematically, and the mathematical formulation is given below. The first substep is the gas–liquid equilibrium of A at the gas–liquid interface,

$$ A(g) \xrightarrow{H} A(aq) $$

(4)

where $H$ is Henry’s law constant. Assuming the gas–liquid equilibrium of A at the interface, the following relation of the equilibrium state of A is obtained,

$$ C_A^{int} = \frac{p_A}{H} $$

(5)

where $C_A^{int}$ is the equilibrium concentration of A at the interface. Inserting the state of an ideal gas into Eq. (5) leads to the partition coefficient of A between the air and the water phases, $K$ [29],

$$ K = \frac{C_A^G}{C_A^{int}} = \frac{H}{RT} $$

(6)
The equilibrium concentration of \( A \) at the interface, \( C_{\text{int}}^A \), can be evaluated by giving the values of \( H \), \( C_G^A \) (or, \( p_A \)), and \( T \).

For example, the partition coefficient of CO\(_2\) between the gas and liquid is estimated as \( K \approx 1.2 \) at 298.2 K [30], and \( C_{\text{int}}^A \) is given by

\[
C_{\text{int}}^A = \frac{C_G^A}{K} = \frac{p_A}{(KRT)}.
\]

By assuming 0.03\% volume fraction of CO\(_2\) in the standard pressure of the atmosphere, \( p_A = 30 \) Pa, at \( T = 293.2 \) K, the equilibrium concentration at the interface is predicted as \( C_{\text{int}}^A \approx 0.01 \) mol\( \cdot \)m\(^{-3} \) by using Eqs. (5) and (6).

The second substep is the gas exchange between the two compartments with an irreversible chemical reaction of \( A \) in turbulent water,

\[
A(\text{aq}) + \text{H}_2\text{O} \xrightarrow{\kappa_A} B(\text{aq}) + \text{H}^+ \tag{7}
\]

where \( \kappa_A \) is the chemical reaction rate. In a well-mixed water compartment without the effect of the molecular diffusion and advection of \( A \) and \( B \), the chemical reaction process of Eq. (7) can be described as

\[
\frac{d}{dt} C_A = -\kappa C_A \tag{8a}
\]

\[
\frac{d}{dt} C_B = \kappa C_A \tag{8b}
\]

where \( \kappa = \kappa_A C_{\text{H}_2\text{O}} \), and \( C_{\text{H}_2\text{O}} \) is concentration of water. Since the water phase is considered as a dilute solution of the gas \( A \), and the variation of the total molar of \( \text{H}_2\text{O} \) by the chemical reaction is sufficiently small compared with that of \( A \), the chemical reaction rate is approximated as a first order of \( C_A \). Using the assumption of the first-order chemical reaction, the chemical reaction rate \( \kappa \) has a unit \([T^{-1}]\).

### 2.2. Governing equations and numerical strategy

A well-developed low-Reynolds-number turbulent water layer with the aquarium chemical reaction is assumed in the directions parallel to the interface, as shown in Fig. 1. The turbulent water flow has a mean flow in the \( x \) direction driven by a well-controlled pressure gradient, and is bounded by a gas–liquid interface at \( z = 0 \), and a solid bottom at \( z = \delta \), respectively. Periodicity is assumed for all the variables in the direction parallel to the interface, therefore, statistical properties of turbulent fluctuations depend only on the distance from the interface, \( z \). The gas–liquid interface is assumed to be flat and shear-free in this study, and the free-slip boundary condition at the interface, \( \frac{\partial u}{\partial z} = \frac{\partial v}{\partial z} = \frac{\partial w}{\partial z} = 0 \) is used. A non-slip boundary condition, \( u = v = w = 0 \), is applied to the bottom boundary. The concentration of the gas \( A \) at the interface is considered uniform, and constant as determined by Eq. (5) based on the gas–liquid equilibrium, while \( C_A^\infty = C_A^\infty \) is imposed at the bottom boundary. This study assumes \( C_A^\infty = 0 \) for simplicity of the problem. Zero concentrations at the interface and the bottom are used for the concentration of \( B \).

It is assumed that fluid in the water phase is incompressible and Newtonian, with constant density, \( \rho \). The physical properties of water, e.g., kinematic viscosity of water, \( \nu \), are also assumed to be constant. The molecular diffusivities of \( A \) and \( B \) in water are considered identical, hence, \( D_A = D_B = D \) is used in the present study. The governing equations of the viscous fluid flow and gas transport are consequently expressed by

\[
\frac{\partial u_i^+}{\partial x_i} = 0 \tag{9a}
\]

\[
\frac{\partial}{\partial t^+} u_i^+ = \frac{\partial}{\partial x_j^+} \left( \frac{1}{\text{Re}_x} \frac{\partial}{\partial x_j^+} u_i^+ - u_j^+ u_i^+ \right) - \frac{\partial p^+}{\partial x_i^+} \tag{9b}
\]
\[\frac{\partial}{\partial t}C_A^+ = \frac{\partial}{\partial x_j^+} \left( \frac{1}{Re_T \cdot Sc} \frac{\partial}{\partial x_j^+} C_A^+ - u_j^+ C_A^+ \right) - K \cdot C_A^+ \]  
(9c)

\[\frac{\partial}{\partial t}C_B^+ = \frac{\partial}{\partial x_j^+} \left( \frac{1}{Re_T \cdot Sc} \frac{\partial}{\partial x_j^+} C_B^+ - u_j^+ C_B^+ \right) + K \cdot C_A^+ \]  
(9d)

with the nondimensionalization

\[u_i^+ = \frac{u_i}{u_T}, \quad p^+ = \frac{p}{\rho u_T^2}, \quad C_A^+ = \frac{C_A}{\Delta C_A}, \quad C_B^+ = \frac{C_B}{\Delta C_A}, \quad x_i^+ = \frac{x_i}{\delta}, \quad t^+ = \frac{t}{\delta/u_T} \]  
(10)

where \(u_i\) (\(i = 1, 2, 3\)) is the velocity, \(p\) is the pressure, \(C_A\) and \(C_B\) are the concentrations of A and B, \(t\) is time, and \(x_i\) is three-dimensional coordinate, respectively. These governing equations are normalized by using the shear velocity at the bottom, \(u_T\), kinematic viscosity of water, \(\nu\), height of the water layer, \(\delta\), and the concentration difference of A between the interface and the bottom of the water compartment, \(\Delta C_A = C_A^{\infty} - C_A^\circ\), as shown in Eq. (10). The subscripts 1, 2, and 3 denote the streamwise, spanwise, and interface-normal directions, respectively, corresponding to the \(x, y,\) and \(z\) directions, and \(u_1 = u, u_2 = v, u_3 = w\) are used to signify the velocity component in the discussions below.

These governing equations involve three nondimensional parameters,

\[Re_T = \frac{u_T}{\nu/\delta} \quad (11a)\]

\[Sc = \frac{\nu}{D} \quad (11b)\]

\[K = \frac{\kappa}{u_T/\delta} \quad (11c)\]

The first is the Reynolds number, the second is the Schmidt number, and the last is the nondimensional chemical reaction rate. The Reynolds number, \(Re_T\), is set to be 150, which corresponds to the Reynolds number defined by the bulk-mean velocity of water, \(U_m \equiv (1/\delta) \int_0^\delta u(z) \, dz\), and \(Re_m \equiv U_m/\nu \approx 2300\). Here, \(\langle \cdot \rangle\) denotes the ensemble average, as introduced in Eq. (15) later. The Schmidt number is varied between \(Sc = 2^0 = 1\) and \(2^3 = 8\) to observe the effect of the molecular diffusivities of A and B in water on the gas exchange processes at the interface. The nondimensional chemical reaction rate this study deals with is varied between \(10^{-\infty} \leq K \leq 10^1\), choosing six values of \(K = 10^{-\infty} \approx 0\), and \(10^n\) with \(n = -3\) to 1, to discuss the effect of the chemical reaction rate on the gas exchange processes. Hence, 24 cases of the combinations of \(Sc\) and \(K\) have been considered in the present study to examine the effects of the Schmidt number and the chemical reaction rate on the gas exchange mechanisms across the interface.

The present numerical experiments employ the same numerical procedures used in the previous study to solve the governing equations (9a)–(9d) [24]. The governing equations are discretized by a finite difference method on a Cartesian staggered grid using a second-order central difference in space for the all terms. The discretized governing equations are advanced by a third-order Runge–Kutta method for the nonlinear and the source/sink terms and a second-order Crank–Nicolson method for the linear terms [31], combined with the four-substep fractional time step strategy [32]. A Helmholtz-type partially differential equation of the velocity, concentrations and pressure are solved by a combination of the fast Fourier transforms (FFT) and the Gaussian elimination for a tridiagonal linear equations [33].

A total of \(7.15 \times 10^6\) (= \(256 \times 288 \times 97\)) grid points is used to discretize the governing equations in the water compartment whose sizes are \(L_x \times L_y \times \delta = 5 \pi \delta \times 2.5 \pi \delta \times \delta\), or, \(L_x^+ \times L_y^+ \times \delta^+ = 2356 \times 1178 \times 150\), where superscript + denotes that the variable is nondimensionalized by \(u_T\) and \(\nu\). The sizes of the water compartment are confirmed large enough in the \(x\) and \(y\) directions to impose the periodic boundary conditions for the all variables [24], however, suitability of the sizes of the water compartment is verified later in this study. The grid spacings in both the \(x\) and \(y\) directions are equidistant, and \(\Delta x^+ \approx 9.20\), and \(\Delta y^+ \approx 4.09\). The grid spacing in the \(z\) direction is determined by a hyperbolic tangent function to concentrate the grid points in both the regions near the bottom and the interface. The minimum and maximum spacings are \(\Delta z^+ \approx 0.183\) and \(3.49\), respectively. Suitability of the grid resolution of numerical data for \(Sc = 1\) is confirmed by the previous study [24]. Suitability of the grid resolution for the other Schmidt numbers is verified by observing nonphysical profiles of spectra of the fluctuations of the concentration fields in large wavenumber space, as shown later.

2.3. Effect of the Schmidt number

It should be mentioned here that the Schmidt number of a gaseous material in water is generally in the order of \(10^2\)–\(10^3\). For example, the molecular diffusivity of \(CO_2\) has been reported as about \(2.02 \times 10^{-9} \, m^2 \, s^{-1}\) at 298.2 K by Zeeby [34] based on his molecular dynamics simulations. Considering the kinematic viscosity of water at the same temperature of \(8.90 \times 10^{-7} \, m^2 \, s^{-1}\) [35], the Schmidt number is approximately \(4.4 \times 10^2\). Also, \(Sc \approx 3.6 \times 10^2\) is obtained in the case of the oxygen exchange across the interface at 298.2 K [36]. The Schmidt numbers this study considers, \(1 \leq Sc \leq 8\), appear to be two to three orders of magnitude smaller than the actual Schmidt numbers of the actual gases. The use of one-digit Schmidt numbers is inevitable in this study, since employing the actual Schmidt numbers of the order of \(10^2\) or larger requires an enormous number of grid points, and computational resources to resolve all the essential scales of the concentration
fluctuations. The effect of the Schmidt number on physics of the gas exchange is observed carefully to extrapolate the results from the present DNS toward the larger Schmidt numbers. This effort will offset the major limitation of this study, in which \( \text{Sc} \sim \mathcal{O}(10^5) \) is used to avoid huge computational resources for the present numerical experiments.

2.4. Gas transfer velocity

The concept of the gas transfer velocity is often introduced to quantify the gas exchange rate at the gas–liquid interface. The gas transfer velocity, \( k_L \), is defined by

\[
Q_A = k_L (C_A^{\text{int}} - C_A^\infty) = k_L \left( \frac{C_A^G}{K} - C_A^\infty \right)
\]

where \( Q_A \) is the gas flux of A at a unit area of the interface and time. The dimension of \( k_L \) is \( [\text{LT}^{-1}] \), therefore, this quantity has the same dimension of the velocity, and is referred to as the “gas transfer velocity.” By applying Fick’s law of the molecular diffusion at the interface, the gas transfer velocity is expressed as

\[
k_L = \frac{D}{\Delta C_A} \frac{\partial}{\partial z} \langle C_A \rangle \bigg|_{z=0}
\]

where \( \langle C_A \rangle \) is the ensemble average of \( C_A \) based on the definition shown in Eq. (15). This equation indicates that the gas transfer velocity is proportional to the concentration gradient of A at the interface. Nondimensionalization of Eq. (13) using the nondimensional concentration of A and z coordinate, \( C_A^* \) and \( z^* \), leads to a definition of the Sherwood number,

\[
\text{Sh} = \frac{k_D}{D} = \left| \frac{\partial}{\partial z^*} \langle C_A^* \rangle \right|_{z^*=0}
\]

Eq. (14) shows that the Sherwood number is equivalent to the nondimensional concentration gradient at the interface. Introducing the nondimensional parameter is beneficial to compare the gas transfer velocity in a different experimental and numerical conditions [22,24].

3. Results

In the following discussions, a variable \( f \) is decomposed into its time-space average between \( t = 0 \) to \( T_A \) over the \( x-y \) plane, and fluctuation around the average like \( f = \langle f \rangle + f^\prime \), where \( \langle f \rangle \) is defined by

\[
\langle f \rangle (z) = \frac{1}{T_A} \int_0^{T_A} \left( \frac{1}{L_x L_y} \int_0^{L_x} \int_0^{L_y} f(x, y, z, t) \, dx \, dy \right) \, dt
\]

This study uses sufficiently long time duration for computing turbulence statistics, \( T_A^+ = T_A u_T^2 / v \geq 4500 \), which is more than 30 times that of the characteristic time scale of the surface-renewal eddies at the interface [24] to obtain fully-converged turbulence statistics.

3.1. Effect of the Schmidt number on the gas exchange mechanisms in the case of zero chemical reaction rate

This section discusses the effect of the Schmidt number on the gas exchange mechanisms in the case of zero chemical reaction rate, \( K = 10^{-\infty} \). The discussions are helpful to understand fundamental physicochemical processes of the gas exchange across the interface. In addition, the statistical analyses of the concentration fluctuations, and the turbulent contribution of the gas flux without the chemical reaction can also be used for validations of the grid resolution and suitability of the compartment sizes of the water phase.

Figs. 2(a)–2(d) show instantaneous concentration profiles of A in the \( y-z \) plane, which is perpendicular to the mean flow in water for \( \text{Sc} = 1–8 \) in the case of zero chemical reaction rate \( (K = 10^{-\infty}) \) to shed light on the effect of the Schmidt number on turbulent transport of A in water. The four plots show the concentration profiles of A in the whole of the computational domain, hence, the sizes of the snapshots are \( W^+ = 1178 \) in width, and \( H^+ = 150 \) in height. The comparison of the concentration profiles demonstrates that turbulent mixing of the gas A in water is accelerated as the Schmidt number increases. The contrast of these black-and-white mappings becomes more uniform in grey except in the region close to the interface (upper boundaries of these snapshots) and the bottom (lower boundaries). It is also very clear from these mappings that the presence of the small-scale concentration fluctuations is more visible as the Schmidt number increases. The emphasis of the fine-scale fluctuations of the concentration of \( C_A \) by increasing the Schmidt number is demonstrated more clearly in Fig. 3. These snapshots are enlarged images of the concentration profiles depicted in Figs. 2(a)–2(d), whose sizes are \( W^+ = 400 \) in width and \( H^+ = 150 \) in height, exhibiting intensification of the fine-scale concentration fluctuations by increasing the Schmidt number.
One-dimensional spectra for the concentration fluctuations, and co-spectra of $w'$ and $C_A'$, are computed in both the $x$ and $y$ directions to elucidate the effect of the Schmidt number on the concentration fluctuation in a more statistical manner. Here, the spectra and the co-spectra are defined by

$$E_{AA}(k_\alpha) = \frac{1}{2\pi} \left\{ \mathcal{F}_\alpha(C_A') \mathcal{F}_\alpha^*(C_A') \right\}$$  \hspace{1cm} (16a)$$

$$C_{wA}(k_\alpha) = \frac{1}{2\pi} \mathcal{R} \left\{ \mathcal{F}_\alpha(w') \mathcal{F}_\alpha^*(C_A') \right\}$$  \hspace{1cm} (16b)$$

where $\mathcal{F}_\alpha(.)$ denotes the Fourier transform in the $\alpha (=1, 2)$ direction, $\mathcal{R}(.)$ shows the real part of a complex number, and the superscript * signifies the complex conjugate. The spectra satisfy the following relation,
\[
\langle C'_A C'_A \rangle = \int_0^\infty E_{AA}(k_1) \, dk_1 = \int_0^\infty k_1 E_{AA}(k_1) \, d(\ln k_1)
\]
\[
= \int_0^\infty E_{AA}(k_2) \, dk_2 = \int_0^\infty k_2 E_{AA}(k_2) \, d(\ln k_2)
\]

(17)

Similarly, the co-spectra, \( C_{wA} \), satisfy
\[
\langle w' C'_A \rangle = \int_0^\infty C_{wA}(k_1) \, dk_1 = \int_0^\infty k_1 C_{wA}(k_1) \, d(\ln k_1)
\]
\[
= \int_0^\infty C_{wA}(k_2) \, dk_2 = \int_0^\infty k_2 C_{wA}(k_2) \, d(\ln k_2)
\]

(18)

where \( w'C'_A \) is the turbulent gas flux of \( A \) in the direction perpendicular to the interface. This quantity appears in the time-space averaged gas transfer equation in Eq. (22) as introduced later, and is one of the important turbulence statistics necessary to understand the gas exchange processes.

Figs. 4(a) and 4(b) show the one-dimensional spectra of the concentration fluctuations at \( z^+ = 15, 30, \) and 75 (\( z^+ = 0.1, 0.2, \) and 0.5) in both the \( x \) and \( y \) directions. These spectra are normalized by \( \langle C'_A C'_A \rangle \) at the individual locations. This figure illustrates the plots of the relation between \( (k_\alpha \delta) E_{AA}(k_\alpha) \) and \( \log(k_\alpha) (\alpha = 1, 2) \) to compare the effect of the Schmidt number on a semi-logarithmic chart, based on the relation shown in Eq. (17). Fig. 4 shows clearly that the contribution of the small-scale concentration fluctuations becomes significant as the Schmidt number increases. For example, \( (k_1 \delta) E_{AA}(k_1) \) evaluated at \( z^+ = 15 \) reaches a maximum at \( k_1 \delta = 2.8 \) for \( Sc = 1 \), \( k_1 \delta = 6.0 \) for \( Sc = 2 \), and \( k_1 \delta \approx 8 \) for \( Sc = 4 \) and 8. Also, it is observed easily from Fig. 4(b) that \( (k_2 \delta) E_{AA}(k_2) \) at \( z^+ = 15 \) decays sufficiently small in the high wavenumber region, \( k_2 \delta > 40 \) for \( Sc = 1 \), and the value is in the order of \( 10^{-6} \). On the other hand, \( (k_2 \delta) E_{AA}(k_2) \) at \( k_2 \delta = 40 \) for \( Sc = 8 \) is not small enough compared with that for \( Sc = 1 \), and the value is 0.055. Although the decay of the spectra seems to be slower as the Schmidt number becomes larger, the spectra of \( C'_A \) fall to zero at the large wavenumber space for the all Schmidt number cases. The spectra profiles also suggest that the grid resolution needs to be fine enough as the Schmidt number increases, especially in the \( y \) direction to resolve fine-scale concentration fluctuations, and the present computations resolve the fluctuations appropriately.

Figs. 5(a) and 5(b) show the co-spectra \( C_{wA} \) evaluated at \( z^+ = 15, 30 \) and 75, in both the \( x \) and \( y \) directions. These co-spectra are normalized by \( \langle w'C'_A \rangle \) at the individual location, based on the relation shown in Eq. (18). These co-spectra, contrary to the profiles of the spectra of the concentration fluctuations, demonstrate that the effect of the Schmidt number is marginal, indicating very similar profiles for the all Schmidt number cases. The marginal effect of the Schmidt number on the co-spectra profiles suggest that the turbulent gas flux is dominated mainly by the fluid flow structures. These profiles
Fig. 5. Co-spectra of the velocity fluctuations \( w' \) and the concentration fluctuations \( C'_A \) at \( z^+ = 15 \) (left), 30 (middle), and 75 (right) in: (a) \( x \) direction, and (b) \( y \) direction.

Further indicate that the drop-off of these co-spectra is sufficient in the high wavenumber space \( k_1 \) and \( k_2 \) increase, and nonphysical profiles of the co-spectra are not observed in these profiles.

The two-point correlations of \( C'_A \) in the \( x \) and \( y \) are defined by

\[
C_{AA}(x) = \frac{\langle C'_A(x_0 + x, y_0, z) C'_A(x_0, y_0, z) \rangle}{(C_{rms}^A)^2} \tag{19a}
\]

\[
C_{AA}(y) = \frac{\langle C'_A(x_0, y_0 + y, z) C'_A(x_0, y_0, z) \rangle}{(C_{rms}^A)^2} \tag{19b}
\]

where \( 0 \leq x_0 < L_x \), and \( 0 \leq y_0 < L_y \), and \( C_{rms}^A \) is the root-mean-square of \( C'_A \). The two-point correlations are computed from the spectra of \( C'_A \) shown in Fig. 5 using the Weiner–Khinchin theorem [37]. Figs. 6(a)–6(d) show the profiles of the two-point correlation of the concentration fluctuations \( C'_A \) at \( z^+ = 15, 30, \) and 75 in the \( x \) and \( y \) directions, respectively. The profiles exhibit that these two-point correlations fall to zero as \( x \) and \( y \) increase toward the largest separations, \( x^+ = 2.5\pi \delta^+ \approx 1178 \), and \( y^+ = 1.25\pi \delta^+ \approx 589 \). Also, it is found from these plots that the effect of the Schmidt number on the structures of the concentration fields appears in the length scales of about \( x^+ < 100 \), and \( y^+ < 200 \). The length scales of \( x^+ \approx 100 \) and \( y^+ \approx 200 \) correspond to the wavenumbers \( k_1 \delta = k_2 \delta \approx 11.8 \), and the spectra of \( C'_A \) at these wavenumbers are altered drastically by the Schmidt number, as already shown in Figs. 4(a) and 4(b). The drop-off of the two-point correlation to zero Fig. 6 indicates is satisfactory, and interactions of the concentration fluctuations between two points of the largest separation do not exist. The sizes of the compartment in the water phase this study uses are considered large enough in both the \( x \) and \( y \) directions to cover the largest flow structures. Together with the profiles of the spectra and co-spectra, the current grid points resolve all the essential scales of the concentration fluctuations, while the largest flow structures are not minced by an inappropriateness of the sizes of the computational compartment.

3.2. Gas exchange rate

Figs. 7(a)–7(d) show the effect of the chemical reaction rate \( K \) on the mean concentration profiles of the gas A in turbulent water for \( Sc = 1, \ 2, \ 4, \ ) and 8, respectively. Comparison of the concentration profiles between \( K = 10^{-\infty} \) and \( K = 10^{-3} \) suggests that the effect of the chemical reaction on the gas exchange at the interface is considered extremely small. On the other hand, the concentrations of A in turbulent bulk water at about \( z^+ > 0.2 \) for \( K = 10^1 \) fall to zero for the all Schmidt number cases, exhibiting extreme difference of the profiles for \( K = 10^{-\infty} \) and \( 10^{-3} \). These concentration profiles of A for \( K = 10^1 \) suggest that the time scale of the chemical reaction is short enough, compared with that of the turbulent gas exchange by the surface-renewal motions from the interface toward turbulent bulk. The fast chemical reaction consumes a considerable portion of the gas A during its transport processes within the turbulent boundary layer below the interface, and the concentration of A become very small outside of the interfacial turbulent boundary layer.
Fig. 6. One-point correlation of the concentration fluctuations of A in water turbulence at $z^+ = 15$ (left), 30 (middle), and 75 (right) in: (a) $x$ direction, and (b) $y$ direction.

Fig. 7. The effect of the chemical reaction rate on the concentration profiles of A in turbulent water in the cases of: (a) $Sc = 1$; (b) $Sc = 2$; (c) $Sc = 4$; and (d) $Sc = 8$.

We need a quantitative discussion of the time scales of the surface-renewal motions, $T_S$, and that of the chemical reaction, $T_C$, to examine the effect of the chemical reaction on the gas exchange processes across the interface. The two time scales are defined by the following equations

\begin{align}
    T_S &= V / \Lambda \\
    T_C &= 1 / \kappa
\end{align}

where $V$ and $\Lambda$ are the characteristic velocity and length scales of the surface-renewal eddies [38], respectively. The details of the estimation of the time scale $T_S$ have been discussed in the previous study [24]. The results of the previous
Fig. 8. The effect of the chemical reaction rate on the instantaneous concentration profiles of A in turbulent water in the cases of: (a) $K = 10^{-3}$; (b) $K = 10^{-2}$; (c) $K = 10^{-1}$; (d) $K = 10^0$; and (e) $K = 10^1$ for Sc = 4.

The statistical analysis demonstrate that the time scale of the surface-renewal motions is evaluated as $\overline{T_S} \equiv T_S u / \delta \approx 0.664$. We understand easily from Eqs. (20a) and (20b) that the two time scale is approximately the same for $K = 10^0$, because of $\overline{T_C} \equiv 1/K = u / \kappa \delta = 1.0$. It is also evident that the time scale of the chemical reaction overwhelmingly faster that of the surface-renewal in the case of $K = 10^1$ (i.e., $\overline{T_C} = 0.1$). A significantly large part of the gas A is consumed very quickly by the fast chemical reaction of $K = 10^1$, during its exchange processes very near the interface. The time scale of the chemical reaction is comparable, or longer than that of the surface-renewal for the other cases of $K$, the gas A is not consumed so quickly in its exchange process, and the concentration profiles of A is non-zero in turbulent bulk.

Figs. 8(a)–8(e) illustrate an example of the effect of the chemical reaction rate on the instantaneous profiles of A for Sc = 4 in the $y$–$z$ plane, which is perpendicular to the mean flow of water, to show the trend found in Fig. 7 in a more visible manner. These plots of the concentration profiles cover the domain sizes of $W^+ = 589$ in width, and $H^+ = 150$ in height. These snapshots of the instantaneous concentration profiles are easy to compare with each other, since the computations have been performed using the same fluid velocity profiles. The result for $K = 10^{-\infty}$ is omitted from this figure, since the profile of A is almost identical to the case of $K = 10^{-3}$, in which zero-concentration profile of B is achieved in the water compartment. The statistical observations discussed above are confirmed qualitatively from the instantaneous profiles of the concentration of A in turbulent water. The disappearance of A in turbulent water is significant as the chemical
reaction rate increases, and the substance A survives only in the region very close to the interface for $K = 10^1$. We observe essentially the same instantaneous profiles of A in turbulent water for the other Schmidt number cases.

Fig. 7 also demonstrates that the gas exchange rate at the interface, which is proportional to the nondimensional concentration gradient at the interface as shown in Eq. (14), increases with the increase the chemical reaction rate for the all Schmidt number case. Fig. 9 illustrates the relation between the chemical reaction rate $K$ and the nondimensional gas exchange rate, $Sh$, to clarify the effect of the chemical reaction on the gas exchange rate. The dashed lines in this figure signify the Sherwood number in the case of $K = 10^{-\infty}$. This graph shows that the effect of the chemical reaction enhances the gas exchange across the interface, as indicated in Fig. 7, and increases the gas exchange rate for $Sc = 1$–8 span by approximately one order by increasing the chemical reaction rate $10^4$ times from $K = 10^{-3}$ to $10^1$. The relation also indicates that the effect of the chemical reaction in water should be considered exactly for evaluating the gas exchange rate at the interface, especially as the gas is highly reactive in water, since the exchange rate is very sensitive to the chemical reaction rate.

### 3.3. Relation between the Schmidt number and the gas exchange rate

The surface-renewal model for approximating the gas exchange processes at the interface predicts that the gas exchange rate is proportional to the molecular diffusivity of a gas, $k_l \propto (D/T_S)^{1/2}$ [38]. Nondimensionalizing this equation leads to

$$ShSc^{-n} = \alpha$$

(21)

where $\alpha$ is a constant, and $n = 1/2$ has been predicted based on the model [24,38]. This relation is often used to estimate the gas exchange rate of a gas between air and water using a reference value of the exchange rate $Sh_0$ at $Sc_0$, as $Sh = Sh_0(Sc/Sc_0)^{1/2}$ [7]. The validation has not been covered in the previous study [24], and it should be performed here to extrapolate the value of the gas exchange rate from $Sc \sim O(10^0)$ toward $O(10^2)$ accurately, in particular under presence of the chemical reaction.

Fig. 10 illustrates the relation between the Schmidt number and the nondimensional gas exchange rate for the six chemical reaction rates. The lines in this figure indicate the best-fit results of the present numerical experiments using the relation of Eq. (21). Table 1 summarizes the values of $\alpha$ and $n$ for the individual chemical reaction rates obtained

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|}
\hline
$K$ & $\alpha$ & $n$ \\
\hline
$10^{-3}$ & 0.491 & 0.472 \\
$10^{-2}$ & 0.518 & 0.472 \\
$10^{-1}$ & 0.614 & 0.472 \\
$10^0$ & 0.550 & 0.472 \\
$10^1$ & 0.483 & 0.472 \\
\hline
\end{tabular}
\caption{Values of $\alpha$ and $n$ for the individual chemical reaction rates.}
\end{table}
Table 1
A best-fit correlation between Sh and Sc using the correlation shown in Eq. (21).

<table>
<thead>
<tr>
<th>K</th>
<th>α</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>10^{-∞}</td>
<td>4.66</td>
<td>0.472</td>
</tr>
<tr>
<td>10^{-3}</td>
<td>4.73</td>
<td>0.489</td>
</tr>
<tr>
<td>10^{-2}</td>
<td>5.13</td>
<td>0.550</td>
</tr>
<tr>
<td>10^{-1}</td>
<td>8.07</td>
<td>0.614</td>
</tr>
<tr>
<td>10^{0}</td>
<td>15.8</td>
<td>0.518</td>
</tr>
<tr>
<td>10^{1}</td>
<td>39.0</td>
<td>0.491</td>
</tr>
</tbody>
</table>

by the least-square method. The same values of n are also indicated in Fig. 10. Table 1 indicates that the exponent of Eq. (21) is n = 0.472 for $K = 10^{-∞}$, which agrees well with $n = 1/2$ predicted by the model developed by Dankwerts [38]. The exponent predicted by the present numerical study is very close to the results of the DNS study of gas transport at $Re_t = 300$ ($Re_m = 5090$) and $1 \leq Sc \leq 8$ by Kermani et al. [23]. Wang and Lu [26], and Calmet and Magnaudet [25,27] employed a large-eddy simulation (LES) technique for a turbulent water layer, and have discussed the relation between the gas exchange rate and the molecular diffusivity of a scalar across the interface without considering an aquarium chemical reaction. Their results exhibit suitability of $n = 1/2$ at a high Schmidt number up to $Sc = 200$.

Table 1 also shows that the exponent n is very close to 1/2 in the cases of $K = 10^0$, and $10^1$, in which the time scale of the aquarium chemical reaction is equivalent, or faster than that of the surface-renewal eddies. A deviation from the surface-renewal model is observed for the gas exchange processes across the interface in the cases of $K = 10^{-2}$ and $10^{-1}$, in which the effect of the chemical reaction is not negligible, but the time scale of the chemical reaction is not fast enough to overwhelm that of the surface-renewal eddies. The results in Fig. 10 show that the surface-renewal model is expected appropriate to extrapolate the effect of the Schmidt number on the gas exchange rate from $Sc \sim O(10^0)$ toward $O(10^2)$, using Eq. (21) with $n = 1/2$, in both the limits of the zero and infinite chemical reaction rate. It is also demonstrated that careful extrapolation of the gas exchange rate using the relation $Sh \propto Sc^{1/2}$ is required in a case of moderate chemical reaction rate.

Here, it is revealed successfully that the present predictions by DNS can extrapolate the Sherwood number to the criteria of the larger Schmidt number and the chemical reaction limits, using the results in Figs. 9 and 10. The extrapolations of the effect of the Schmidt number to larger values, e.g., $Sc > O(10^2)$, can be applied by using Eq. (21) with the values in Table 1. The exponent n in the cases of the zero and infinite chemical reaction limits is very close to 1/2, and the surface-renewal model provides a good approximation for predicting the gas exchange rate in these cases.

### 3.4. Effect of the chemical reaction on turbulent gas flux

Taking time-space average of the transport equation of the gas A with a decomposition of the concentration and velocities into their mean and fluctuating parts, the following equation is obtained

$$\langle w^+ C_A^+ \rangle_{\text{Turb}} - \frac{1}{Re_t Sc} \frac{\partial}{\partial z^+} (C_A^+) = -\left\{ K \int_0^{z^+} \langle C_A^+ \rangle dz^+ + \frac{1}{Re_t Sc} \frac{\partial}{\partial z^+} (C_A^+) \right\}_{z^+ = 0} \quad \text{(22)}$$

It is obvious from this equation that the total gas flux is constant in the case $K = 10^{-∞}$ [22], and the constant should be $k^+_L = k_L/(Re_t Sc)$ using the definition of the Sherwood number in Eq. (14). The total flux is not constant, and decreases with increasing the distance $z$ by the first term of the right-hand side of Eq. (22) if the chemical reaction rate is not zero.

Profiles of the turbulent gas flux in Eq. (22) are important in establishing a simple, and predictive turbulent closures for estimating the gas exchange rate at the interface at the very high Schmidt numbers [39]. Figs. 11(a)–11(d) illustrate the effect of the chemical reaction rate on the profiles of turbulent and viscous contributions of the gas fluxes in the region close to the interface $0 \leq z^+ = u_{zt}/v \leq 50$, for $Sc = 1–8$, respectively. It is easily observed from these graphs that increasing the chemical reaction rate enhances the viscous contribution, especially in the layer below the interface, $z^+ < 1$ (or, $z^+ < 1/150$). Fig. 11 also shows that the enhancement of the turbulent contribution is rather inconspicuous, compared with the enhancement of the viscous contribution. It is clear that the role of the molecular diffusion on the gas A exchange at the interface is important, especially under presence of the fast chemical reaction.

The profiles of the turbulent and viscous contributions of the gas flux also suggest that the turbulent closures for the gas exchange without the chemical reaction are applicable to the cases of non-zero chemical reaction rates, without drastic modification of their mathematical structures. One of the reasons for this speculation is that the turbulent gas flux is proportional to $z^{-2}$ at the interface for the all chemical reaction rate. This asymptotic behaviour of the turbulent and viscous contributions of the gas flux indicates that the eddy diffusivity is proportional to $z^{-2}$ [26], since it is defined by
Fig. 11. The effect of the chemical reaction rate on the contributions of the turbulent and viscous parts of turbulent gas flux for: (a) $Sc = 1$; (b) $Sc = 2$; (c) $Sc = 4$; and (d) $Sc = 8$. The dashed lines indicate the relation that the turbulent gas flux is proportional to $z^+^2$.

\[
D^+_T \equiv \frac{D_T}{\nu} = -\text{Re} \left( \frac{\langle w'C_A' \rangle}{\partial \langle C_A \rangle / \partial z} \right)
\]

(23)

Figs. 12(a)–12(d) depict the profiles of the eddy diffusivity of the gas A against $z^+$ for the Schmidt number cases of $Sc = 1–8$, respectively. This figure confirms that $D^+_T$ is proportional to $z^+^2$ at the near-interface region $z^+ \geq 10$ for the all Schmidt number cases. This figure also indicates that the asymptotic behaviour is not altered by the presence of the chemical reaction. The same asymptotic behaviour has been reported by Wang and Lu\[26\] in turbulent water flows with/without thermal stratification at high Prandtl numbers up to $Pr = 200$ using the LES technique. Also, Suga and Kubo\[39\] obtain the same asymptotic behaviour of the eddy diffusivity at the interface by their theoretical consideration in a turbulent open-channel flow. The predictions of the gas exchange rates across the interface based on the turbulent closure developed by Suga and Kubo agree well with the laboratory experiments by Komori et al.\[40,41\], and Rashidi et al.\[42\] at the high Schmidt numbers up to $10^3$. It could be speculated from the results of the present numerical study, together with the results in Refs.\[26\] and \[39\], that the essential mechanisms of the gas exchange across the interface is not varied drastically by the presence of the chemical reaction.

4. Discussion

Predicting the concentration of the degradation product of B is an important issue on chemodynamics in the environment, especially if it has ecotoxicity, or serious impacts on the ecosystem and human being. Mechanisms of the chemical reaction processes in water, combined with turbulent gas exchange and mixing near the interface, should be modelled appropriately in environmental transport problems. The numerical modelling proposed in this study can predict three-dimensional profiles of B in the water compartment, and the effect of the turbulent mixing in water on the production of B is examined based on the numerical data represented in this study.

Figs. 13(a)–13(d) illustrate the effect of the chemical reaction rate on the mean concentration profiles of B for $Sc = 1–8$, respectively. The profiles of $\langle C_B' \rangle$ for $K = 10^{-3}$ are very small in the entire region, which stay in the order of approximately $10^{-3}$ or less for $Sc = 1$, and $10^{-2}$ or less for $Sc = 8$. It is also revealed that the profiles of $\langle C_B' \rangle$ for $K = 10^1$ are different with those for the other chemical reaction rates. The profiles of $\langle C_B' \rangle$ for $K = 10^1$ have clear peak in the near-interface region, $z^+ \approx 0.080$ for $Sc = 1$, 0.059 for $Sc = 2$, 0.043 for $Sc = 4$, and 0.030 for $Sc = 8$, however, the other profiles are rather flat in turbulent bulk at $0.1 < z^+ < 0.9$ for the all Schmidt number cases. The difference is caused by presence of very fast chemical reaction of $K = 10^1$, whose time scale of the chemical reaction is overwhelmingly shorter than that of the surface-renewal motions, and the effect of the chemical reaction on the production of B is very active in the layer below the interface.
Fig. 12. The effect of the chemical reaction rate on the profiles of the eddy diffusivity: (a) Sc = 1; (b) Sc = 2; (c) Sc = 4; and (d) Sc = 8. The dashed lines indicate the relation that the eddy diffusivity is proportional to $z^2$.

Fig. 13. The effect of the chemical reaction rate on the concentration profiles of B in turbulent water in the cases of: (a) Sc = 1; (b) Sc = 2; (c) Sc = 4; and (d) Sc = 8.

Figs. 14(a)–14(e) illustrate an example of the effect of the chemical reaction rate on the instantaneous profiles of B for Sc = 4 in the $y$–$z$ plane to show the trend found in Fig. 13 visually. These plots of the concentration profiles cover the domain sizes of $W^+ = 589$ in width, and $H^+ = 150$ in height. These snapshots of the instantaneous concentration profiles are easy to compare with each other and those exhibited in Fig. 8, since the computations have been performed using the same fluid velocity profiles. The snapshots show that the production of B in turbulent water is activated by the increase of
Fig. 14. The effect of the chemical reaction rate on the instantaneous concentration profiles of B in turbulent water in the cases of: (a) $K = 10^{-3}$; (b) $K = 10^{-2}$; (c) $K = 10^{-1}$; (d) $K = 10^0$; and (e) $K = 10^1$ for $Sc = 4$.

The chemical reaction rate, and confirm the same trend depicted in Fig. 13. Also, it is clearly observed that the concentration of B in turbulent water is smaller than the equilibrium concentration at the interface, even if the chemical reaction rate is $K = 10^1$. We observe high-concentration spots of B in the region close to the interface in the case of $K = 10^1$ as shown in Fig. 14(e), where the concentration of B is near the equilibrium concentration of A at the interface. The comparison of these snapshots with Fig. 8 suggests that the gas A transferred inside turbulent water reacts very quickly, producing intermittent high-concentration spots of B in the region close to the interface.

It is interesting to quantify the effects of the Schmidt number and the chemical reaction rate on the bulk-mean concentration of B in water. The data could present important information on evaluating the environmental impacts of the degradation product of B, as well as acidification of water by the chemical reaction. Here, the bulk-mean concentration of B is defined by

$$C_B^* = \frac{1}{z^*} \int_0^{z^*} (\rho_B^*) \, dz^*$$

Fig. 15 depicts the effect of the Schmidt and the chemical reaction rate on the bulk-mean concentration $C_B^*$. It is worth to mention here that the bulk-mean concentration of B reaches approximately 0.6 as the chemical reaction rate and the
5. Conclusions and future directions

5.1. Conclusions

This paper proposed a new numerical modelling to assess the environmental chemodynamics of a gaseous material exchanged between air and turbulent water with an aquarium chemical reaction. The study employed an extended concept of a two-compartment model, and separated the gas exchange processes into two physicochemical substeps to approximate mechanisms in the gas exchange between the two compartments in a simple manner. The first was the gas–liquid equilibrium between the air and water phases, \( \text{A(g)} \rightleftharpoons \text{A(aq)} \), and the second a first-order irreversible chemical reaction in turbulent water, \( \text{A(aq)} + \text{H}_2\text{O} \rightarrow \text{B(aq)} + \text{H}^+ \). While zero velocity and uniform concentration of A was considered in the air compartment, a direct numerical simulation (DNS) technique was applied to the non-uniform water compartment to obtain unsteady three-dimensional turbulent velocity and concentration fluctuations in turbulent water. The gas exchange rate of A, and the bulk-mean concentration of B produced by the chemical reaction were evaluated from the results of the present numerical data, as well as several important turbulence statistics. The simulations were performed using different Schmidt numbers between 1 and 8, and six degrees of nondimensional chemical reaction rates between \( 10^{-\infty} \) (\( \approx 0 \)) to \( 10^1 \) at a fixed Reynolds number, \( \text{Re}_\tau = 150 \) \( (\text{Re}_m \approx 2300) \). This study examined the effects of the Schmidt number and the chemical reaction rate on fundamental mechanisms of the gas exchange processes across the interface. Major findings through a series of numerical experiments performed in this study are summarized below.

This study examined the effect of the Schmidt number on the turbulence statistics of the concentration fluctuations and the turbulent contribution of the gas flux of A in the case of zero chemical reaction. The examination showed that fine-scale concentration fluctuations are intensified by increasing the Schmidt number, however, the co-spectra of the turbulent contribution of the gas flux are not altered by the Schmidt number. The examination also validated soundness of the numerical data of the gas exchange processes obtained by the present numerical experiments, confirming that the sufficiently fine grid resolution is applied in a sufficiently large-scale computational compartment of turbulent water.

The effects of the chemical reaction rate and the Schmidt number on the gas exchange rate of the gas A between air and water exhibited that increasing both \( K \) and \( \text{Sc} \) enhance the gas flux at the interface. The effect of the chemical reaction rate on the gas exchange rate was monotonic, and its effect alters the exchange rate drastically, increasing by approximately one order by increasing the chemical reaction rate \( 10^4 \) times from \( K = 10^{-3} \) to \( 10^1 \) at any Schmidt number this study considered. It was also observed that the gas exchange rate can be correlated by Eq. (21), with the exponent of \( n \approx 1/2 \) in the zero and infinite chemical reaction limits. The correlations between the gas exchange rate and the Schmidt number or the chemical reaction rate this study obtained are expected applicable to extrapolate the exchange rate to outside of the criteria of the two parameters this study examined.

This study considered a decomposition of the gas flux of A into the turbulent and viscous contributions, and a comparison of the two contributions were conducted. The examination showed that the viscous contribution to the total gas flux of A is strengthened by the chemical reaction in water especially in the region very close to the interface, while the turbulent contribution is not enhanced drastically compared with the viscous contribution. It is also revealed that the eddy viscosity
is proportional to the square of the distance from the interface, and the asymptotic behaviour is not changed drastically by the chemical reaction rate.

This study further examined the effect of the Schmidt number and the chemical reaction rate on the production mechanisms of $B$ by the aquarium chemical reaction. The bulk-mean concentration of $B$ in water is shown to increase with increasing both $Sc$ and $K$, however, the bulk-mean concentration is shown to approach toward a saturated value, $C_\text{B,ln} \approx 0.6$, in the limits of infinite $Sc$ and $K$. The data is considered useful to assess the impact of the substance of $B$ if it has ecotoxicity. Acidification of water by the chemical reaction is also possible to assess by using the data this study presents.

5.2. Future directions

The following is a list of subjects not covered by the present numerical experiments.

(1) This study did not consider the effect of the Reynolds number on the gas exchange mechanisms with an aquarium chemical reaction, since our attention is rather focused on the effect of the Schmidt number and the chemical reaction rate. We accept the importance of numerical experiments using a different Reynolds numbers to understand fundamental mechanisms of the gas exchange across the interface in a more comprehensive manner.

(2) Also, the Schmidt numbers considered were in the extent of one digit, and the effect on the gas exchange rate of $A$ and the bulk-mean concentration of $B$ are extrapolated. A numerical study using a DNS technique for a large Schmidt number case, e.g., $Sc \approx 100$, is possible to conduct, using finer grid resolution of the order of $1024^3$ by applying a high-performance computing system. Such a super-large-scale computation should be performed to confirm suitability of $Sh \propto Sc^n$, especially $n \approx 1/2$ for $K \to 0$ and $K \to \infty$.

(3) While the chemical reaction this study assumed was irreversible, a reversible chemical reaction, $A(\text{aq}) + H_2O \rightleftharpoons B(\text{aq}) + H^+$, should also be considered for developing further applications of the results from the present numerical works. The gas exchange mechanisms and the chemical reaction processes in turbulent water will be altered if the chemical reaction is reversible, especially in turbulent bulk where the difference between the concentrations of $A$ and $B$ is small. This topic should also be covered by an extension of this study in the near future.

(4) This study considers a well-developed turbulent water layer, and the effect of the air flow above the interface is ignored. Many geophysical and environmental flows with the gas–liquid interface are coupled, with very intense interactions with each other. The effect of a turbulent boundary layer in the air flow cannot be neglected in those cases, and the air–water coupled turbulence with the chemical reactions should also be considered.

6. Conflicts of interest

This study has been conducted without obtaining financial support from outside of the National Institute of Advanced Industrial Science and Technology (AIST). The author does not have any conflicts of interest on the topics covered in this report, and this has been drafted as a scientifically neutral publication, without any intentional bias.

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