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**Air-water gas transfer
velocity scheme**

M. T. Johnson

A numerical scheme to calculate temperature and salinity dependent air-water transfer velocities for any gas

M. T. Johnson

School of Environmental Sciences, University of East Anglia, Norwich, UK

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Correspondence to: M. T. Johnson (martin.johnson@uea.ac.uk)

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Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Abstract

The transfer velocity determines the rate of exchange of a gas across the air-water interface for a given deviation from Henry's law equilibrium between the two phases. In the thin film model of gas exchange, which is commonly used for calculating gas exchange rates from measured concentrations of trace gases in the atmosphere and ocean/freshwaters, the overall transfer is controlled by diffusion-mediated films on either side of the air-water interface. Calculating the total transfer velocity (i.e. including the influence from both molecular layers) requires the Henry's law constant and the Schmidt number of the gas in question, the latter being the ratio of the viscosity of the medium and the molecular diffusivity of the gas in the medium. All of these properties are both temperature and (on the water side) salinity dependent and extensive calculation is required to estimate these properties where not otherwise available. The aim of this work is to standardize the application of the thin film approach to flux calculation from measured and modelled data, to improve comparability, and to provide a numerical framework into which future parameter improvements can be integrated. A detailed numerical scheme is presented for the calculation of the gas and liquid phase transfer velocities (k_a and k_w respectively) and the total transfer velocity, K . The scheme requires only basic physical chemistry data for any gas of interest and calculates K over the full range of temperatures, salinities and wind-speeds observed in and over the ocean. Improved relationships for the wind-speed dependence of k_a and for the salinity-dependence of the gas solubility (Henry's law) are derived. Comparison with alternative schemes and methods for calculating air-sea flux parameters shows good agreement in general but significant improvements under certain conditions. The scheme is provided as a downloadable program in the supplementary material, along with input files containing molecular weight, solubility and structural data for 80 gases of general interest, enabling calculation of the total transfer velocity over ranges of temperature and salinity for each gas.

OSD

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Air-water gas transfer velocity scheme

M. T. Johnson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



1 Introduction

The rate of exchange of a trace gas between the atmosphere and ocean (and other water surfaces) is often calculated from observed or inferred concentrations of the gas of interest, from point measurements in individual field studies or averaged or modelled data used in regional or global budgets of trace gas fluxes. When such calculations are undertaken, the “thin film” model of gas exchange, as applied to the air-sea interface by Liss and Slater (1974) (Fig. 1) is often used. This model assumes that the transfer of gases is controlled by layers of molecular diffusion on either side of the interface. The flux of a gas across the air-water interface can be expressed as that through either of the two molecular layers (Liss and Slater, 1974) (Eq. 1).

$$F = K_a(C_g - K_H C_l) = K_w(C_g/K_H - C_l) \quad (1)$$

Where C_g and C_l are the bulk gas phase and liquid phase concentrations respectively and K_H is the dimensionless gas-over-liquid form of the Henry’s law constant, which is the equilibrium ratio of concentrations in the gas and liquid phase for the gas in question:

$$K_H = \frac{C_{sg}}{C_{sl}} \quad (2)$$

Where C_{sg} and C_{sl} are the interfacial equilibrium concentrations of the gas in question. K_a and K_w are the total transfer velocities for the system as expressed from the point of view of the liquid and gas phase thin films respectively and are each composed of the two single-phase transfer velocities, one representing the contribution of the liquid phase transfer (k_w) and one representing the gas phase transfer (k_a):

$$K_w = \left[\frac{1}{k_w} + \frac{1}{K_H \cdot k_a} \right]^{-1} \quad (3)$$

$$K_a = \left[\frac{1}{k_a} + \frac{K_H}{k_w} \right]^{-1} \quad (4)$$

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Air-water gas transfer velocity schemeM. T. Johnson

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Below a detailed numerical scheme is presented, which allows the calculation of temperature- and (where appropriate) salinity-dependent terms for k_a , k_w and K_H , which in turn allows calculation of total transfer velocities K_a and K_w according to Eqs. (3) and (4) above. This scheme is intended as an improvement over ad-hoc interpretations of transfer velocity calculations applied by individual workers, particularly for estimates of ocean-atmosphere fluxes for less well-studied gases of biogeochemical or other interest. More detailed approaches are often used and are more appropriate for well studied gases such as CO_2 or DMS (dimethylsulfide), where concentration uncertainty is better constrained and physical characteristics of the gases have been determined experimentally.

This paper starts by presenting two new derivations which represent improvements to the current most commonly-used methods for quantifying a) the salinity-dependence of K_H and b) the wind speed dependence of k_a . Following this the full numerical scheme is outlined, with further details provided in Appendix A. The supplementary material contains a full implementation of the scheme, coded in the open-source R software environment, which is freely available for use in other studies.

2 New derivations introduced for this scheme

2.1 Salinity-dependence of Henry's law coefficients

In studies of trace gas exchange to date, where measured data on solubility in seawater has not been available for the particular gas of interest, a blanket 20% solubility decrease has commonly been applied, following Stumm and Morgan (1981), irrespective of the properties of the gas in question. The effect of dissolved salts on gas solubility is a subject that still remains unresolved, with various competing conceptual models being applied to understand and predict the effects of particular dissolved salts on particular gases, such as ion interaction models (e.g., Pitzer, 1991) and scaled particle theory (e.g., Masterton and Lee, 1970). Whatever model best explains the processes

behind the “salting out” (or sometimes “salting in”) of gases, the empirical relationship between solubility and electrolyte concentration can be described according to Setschenow (1889):

$$\text{Log} \frac{\zeta}{\zeta_0} = -K_s \cdot C_{\text{salt}} \quad (5)$$

5 Where ζ and ζ_0 are the solubilities of the non-electrolyte in the salt solution of interest and in pure water, respectively, C_{salt} is the molar concentration of the salt solution and K_s is the empirical Setschenow constant. Here this equation is adapted to represent the salinity-dependent change in solubility as a change in the Henry’s law constant:

$$\text{Log} \frac{K_H}{K_{H,0}} = K_s \cdot S \quad (6)$$

10 Where S is the salinity and $K_{H,0}$ and K_H are the Henry’s law constants in pure water and the saline medium, respectively. Note that the negative sign is removed because the gas-over-liquid form of the Henry’s law constant *increases* with *decreasing* solubility. Thus, if K_s is known for a particular gas in seawater, it is possible to calculate K_H at salinity S , given $K_{H,0}$:

$$15 \quad K_H = K_{H,0} \cdot 10^{(K_s \cdot S)} \quad (7)$$

Extensive experimental data is available for K_s for various gases in single electrolyte solutions, but similar data for real or synthetic seawater is considerably more sparse. What data there is can be reproduced reasonably using the numerical scaled-particle theory model of Masterton (1975). However use of this model requires gas-specific data on the molecular diameter and polarizability, which are not easily available for a wide range of gases and would require additional inputs to the scheme presented here. Therefore, a simpler empirical relationship has been sought.

Rather weak direct (linear) relationships between the “LeBas” liquid molar volume of a gas at its boiling point (V_b) (LeBas, 1915) and K_s were found in single-electrolyte

Air-water gas transfer velocity scheme

M. T. Johnson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Air-water gas transfer
velocity scheme**

M. T. Johnson

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[◀](#)
[▶](#)
[◀](#)
[▶](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)


solutions for for a number of gases by Xie et al. (1997) and for a number of gases and liquids by Ni and Yalkowsky (2003). Ni and Yalkowsky (2003) also found a more reasonable linear relationship between K_s and the octanol-water partitioning coefficients (K_{ow}) of the solutes they investigated.

5 Within scaled particle theory, as applied to the effect of dissolved salts on non-electrolyte solubility, there are two competing processes which can be conceptually related to V_b and (K_{ow}): i) the salting-out effect of the increasing free energy cost of forming “cavities” in the water matrix to accommodate the non-electrolyte molecules with increasing ionic strength and ii) the salting-in effect of the shift in the hydra-
10 tion/dissociation of non-electrolyte molecules in favour of increasing solubility as a result of the increasing polarity of the water-ion matrix with increasing ionic strength (Masterton and Lee, 1970; Masterton, 1975; Zhou and Mopper, 1990; Ni and Yalkowsky, 2003). The former tends to dominate for larger and more hydrophobic molecules and the latter for smaller, more soluble species (Zhou and Mopper, 1990). Molecular size
15 is clearly related to molecular volume, and hydrophobicity/solubility is strongly related to the octanol-water partitioning coefficient.

In the absence of readily available (K_{ow}) data for all gases, a relationship between K_s , Henry’s law (i.e. air-water) solubility and molar volume (which is used elsewhere in the transfer velocity scheme) is sought here. We find the closest fit to the K_s data for
20 real and synthetic seawater by assuming that K_s is a function of the natural logarithm of the molar volume (Eq. 8).

$$K_s = \theta \cdot \ln(V_b) \quad (8)$$

Where θ is a constant of proportionality that is assumed to be solubility-dependent. Using laboratory data on $K_H/K_{H,0}$ for seawater/pure water (Table 1) the Setschenow
25 constant (K_s) has been calculated according to Eq. (6). Then Eq. (8) has been solved for θ , using the additive “Schroeder” method of estimating V_b from molecular structure (Partington, 1949), which has been shown to have a smaller error than the LeBas method when compared to measured values of V_b for a range of compounds (Poling

Air-water gas transfer
velocity scheme

M. T. Johnson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



et al., 2001). The Schroder V_b method is used later and is described in the section outlining the complete numerical scheme (see Table 3). We find a strong, non-linear relationship between θ and $\ln(K_H^\ominus)$ (Fig. 2), where K_H^\ominus is the Henry's law constant in pure water at 25 °C. A cubic model is fitted to this with a root mean square error of 8.76×10^{-5} (Eq. 9). It is logical that K_s should be related to the solubility of the gas along with the molar volume: like the octanol-water partitioning coefficient, the Henry's law constant is strongly related to the polarity of the solute and, as observed by Ni and Yalkowsky (2003): *“salts produce a continuum that is more polar than pure water ... [and] the more non-polar the solute, the more it is influenced by the polarity of the solvent”*.

$$\theta = 7.33532 \times 10^{-04} + 3.39615 \times 10^{-05} \ln K_H^\ominus - 2.40888 \times 10^{-06} (\ln K_H^\ominus)^2 + 1.57114 \times 10^{-07} (\ln K_H^\ominus)^3 \quad (9)$$

Table 1 presents predicted $K_H/K_{H,0}$ data for various gases of interest, compared with measured values, including those used to derive the relationship between θ and $\ln K_H^\ominus$. Note that the deviation from measured values can be attributed both to the error in the derived relationship and also the errors in calculating V_b by the Schroeder method. However, agreement is generally good (less than 5% deviation from measured values in all but six cases). This is a satisfactory level of uncertainty relative to previous approaches, particularly considering that the difference between measured values for the same compound from different studies can vary by this amount or more (e.g. CCl_4 and CH_3Br , Table 1). It is worth noting that the largest deviations are associated with i) the measurement of NH_3 solubility by Sing et al. (1999), and ii) the data of Elliott and Rowland (1993). The study by Sing et al. (1999) was conducted at high temperature and extremely high salinity (Note e, Table 1), and is included only to highlight the steep decrease in salting out effect with increasing solubility (in the absence of more appropriate data for soluble gases in addition to the data points for methanal, Zhou and Mopper, 1990; and H_2O_2 , Bandstra, 2000). The study by Elliott and Rowland

Air-water gas transfer velocity scheme

M. T. Johnson

(1993) has been identified by Moore (2000) as underestimating the salting-out effect for CH_3Cl , and this appears to be supported by the considerably lower value of $K_{\text{H}}/K_{\text{H},0}$ for CH_3Br compared with that measured by De Bruyn and Saltzman (1997). For the above reasons the data of Sing et al. (1999) and Elliott and Rowland (1993) are not

5 included in the data used to fit the model.

2.2 Gas phase transfer velocity, k_a

The gas phase transfer velocity is generally expressed as a function of wind speed, u (or specifically, when considering field measurements, u_{10} – the wind speed at 10 m above the water level). The most commonly used parameterisation in studies of trace gas exchange is that of Duce et al. (1991, Eq. 10), which is derived from micrometeorological theory (detailed below) and which depends on the molecular weight of the gas (MW) as well as wind speed.

$$10 \text{ Duce et al. } k_a = \frac{u_{10}}{770 + 45 \cdot \text{MW}^{1/3}} (\text{m s}^{-1}) \quad (10)$$

This is compared in Fig. 3 with the correlations for k_a presented in Mackay and Yeun (1983), Liss (1973) and Shahin et al. (2002) (Eqs. 11 to 13) for CO_2 and NH_3 (chosen as examples of a relatively insoluble and a soluble gas, respectively).

$$15 \text{ Mackay and Yeun } k_a = 1 \times 10^{-3} + 46.2 \times 10^{-5} \cdot u_* \cdot S_{\text{cA}}^{-2/3} \quad (\text{m s}^{-1}) \quad (11)$$

$$\text{Liss } k_a = 0.005 + 0.21 \cdot u_{10} \quad (\text{cm s}^{-1}) \quad (12)$$

$$\text{Shahin et al. } k_a = D_{\text{A}}^{0.5} \times [0.98 \cdot u_{10} + 1.26] \quad (\text{cm s}^{-1}) \quad (13)$$

20 Where S_{cA} is the Schmidt number and D_{A} is the diffusion coefficient of the gas in air (Eqs. 22 to 25 in the numerical scheme) and u_* is the friction velocity, which is related to the wind speed by the drag coefficient, C_{D} (Eq. 14).

$$C_{\text{D}} = \left(\frac{u_*}{u_{10}} \right)^2 \quad (14)$$

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Mackay and Yeun (1983) apply the wind-speed dependent C_D parameterisation of Smith (1980) when extrapolating their wind tunnel data to environmental conditions (Eq. 15):

$$10^3 \cdot C_D = 0.61 + 0.063 \cdot u_{10} \quad (15)$$

5 An alternative parameterisation for C_D , which is numerically similar to Smith (1980) is that of Large and Pond (1981) (Eq. 16).

$$10^3 \cdot C_D = 1.14 \quad [4 < u_{10} \leq 10 \text{ m s}^{-1}]$$

$$10^3 \cdot C_D = 0.49 + 0.065 \cdot u_{10} \quad [10 < u_{10} < 26 \text{ m s}^{-1}] \quad (16)$$

10 These wind-tunnel-determined or theoretical formulations for k_a all estimate higher values at a given wind speed than the parameterisation of Duce et al. (1991). However, as recognised by Mackay and Yeun (1983), laboratory experiments tend to overestimate transfer velocities due to fetch and roughness effects (due to the non-equilibrium wave field under short fetch) and edge effects (increased turbulence due to wave reflection). Nonetheless a factor of >4 difference between the highest (Shahin et al., 2002) and

15 lowest (Duce et al., 1991) estimates of k_a is a significant uncertainty in terms of quantifying trace gas exchange, particularly as the lowest estimate (rather than a middle case) is most commonly used.

Further investigation of the Duce et al. (1991) parameterisation is therefore warranted. The Duce et al. (1991) k_a is based on the same underlying micrometeorological model as that of Mackay and Yeun (1983). The full derivation can be found in their paper, but their parameterisation can be summarised in terms of S_{cA} , u_* and u_{10} (Eqs. 17 and 18).

$$k_a = \left[\frac{u_{10}}{(u_*)^2} + \left(\frac{5}{u_*} \right) \cdot S_{cA}^{2/3} \right]^{-1} \quad (17)$$

Air-water gas transfer velocity scheme

M. T. Johnson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Where C_D is constant with wind speed with a value of 1.3×10^{-3} , leading to the following relationship between u_* and u_{10} :

$$u_* = u_{10} \cdot \sqrt{1.3 \times 10^{-3}} \quad (18)$$

Therefore it is possible to substitute other C_D parameterisations (e.g. Eqs. 15 or 16) into Eq. (17), to test the sensitivity of k_a to this term. Duce et al. (1991) hold C_D constant as they consider the wind-speed-dependent component of the drag coefficient as minor. However, inclusion of wind-dependent terms for C_D changes k_a substantially at higher wind speeds in the Duce et al. (1991) parameterisation (Fig. 4).

Figure 4 demonstrates that at low wind speeds the selection of the C_D parameterisation is probably not significant, although if applied as is, the Smith (1980) parameterisation (Eq. 15) will tend to underestimate k_a at low to moderate wind speeds relative to the original Duce et al. (1991) equations. However, at high wind speeds the linear Duce et al. (1991) parameterisation leads to apparent substantial underestimation of k_a . It is therefore proposed that the popular Duce et al. (1991) method should be adapted to use a wind speed-dependent term for C_D and furthermore to introduce the “still air” transfer velocity observed by Mackay and Yeun (1983), to better represent the zero wind case (where fetch and roughness effects should not have effected their measurements). The parameterisation derived for the numerical scheme presented here is thus:

$$k_a = 1 \times 10^{-3} + \left[\frac{u_{10}}{u_*^2} + \left(\frac{5}{u_*} \right) \cdot S_{cA}^{2/3} \right]^{-1} \quad (19)$$

where u_* is calculated using Eqs. (14) and (15):

$$u_* = u_{10} \cdot \sqrt{6.1 \times 10^{-4} + 6.3 \times 10^{-5} \cdot u_{10}} \quad (20)$$

This new derivation is compared with other studies in Fig. 5. Note that a relatively recent study has demonstrated that the drag coefficient appears to level out or even start to decrease at wind speeds of greater than $\sim 40 \text{ m s}^{-1}$ (Powell et al., 2003), and

Air-water gas transfer velocity scheme

M. T. Johnson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



this is not accounted for in Eq. (20), so further consideration is necessary if calculating fluxes for extreme wind conditions.

3 Description of the numerical scheme

The numerical scheme was implemented as a program (“K_calcs_T.S.R”) in the R computing environment, which was used for the calculations and plots presented here and is available as supplementary material to the paper (see <http://www.ocean-sci-discuss.net/7/251/2010/osd-7-251-2010-supplement.zip>), along with input data to calculate transfer velocities for 80 trace gases of interest.

3.1 Henry’s law solubility

Data on Henry’s law coefficients in pure water are readily available for most gases, and where solubility data or transfer velocity calculations are presented in this paper, K_H data from the compilation of Henry’s law constants presented by Sander (1999) have been used. These data are presented by Sander (1999) as solubilities in pure water at 25 °C, with units of mol L⁻¹ atm⁻¹. These are converted to dimensionless gas-over-liquid form (Eq. 2), using Eq. (21). Interconversions between various other forms of the Henry’s law (or Bunsen) coefficients are documented by Sander (1999).

$$K_{H,0} = \frac{12.2}{T \cdot H \cdot e\left(\frac{-\Delta_{\text{soln}}H}{R} \times \left[\frac{1}{T} - \frac{1}{298.15}\right]\right)} \quad (21)$$

where $K_{H,0}$ is the dimensionless gas-over-liquid Henry’s law constant in freshwater at given temperature, T (in K); H is the Henry’s law constant in mol L⁻¹ atm⁻¹ at 298.15 K and $-\Delta_{\text{soln}}H$ is the enthalpy change of solution, and $\frac{-\Delta_{\text{soln}}H}{R}$ represents the temperature dependence of the solubility (where R is the gas constant). Values of $\frac{-\Delta_{\text{soln}}H}{R}$ are provided by Sander (1999) and other workers. $K_{H,0}$ can then be scaled for salinity by using Eqs. (7) to (9).

Air-water gas transfer velocity scheme

M. T. Johnson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



3.2 Gas phase transfer velocity, k_a

The gas phase transfer velocity can be calculated using the scheme presented in Eqs. (19) and (20). Equation (19) requires the Schmidt number in air (Eq. 22), which is the ratio of the kinematic viscosity of air (ν_A) and the diffusivity of the gas of interest in air (D_A). ν_A is in turn the ratio of the dynamic viscosity of air (η_A) and the density of air (ρ_A).

$$S_{cA} = \frac{\nu_A}{D_A} = \frac{\eta_A}{\rho_A \cdot D_A} \quad (22)$$

η_A and ρ_A are calculated according to the scheme of Tsilingiris (2008), applicable to saturated air, which is assumed to be representative of the bottom few mm or less of the atmosphere over a water surface.

$$\eta_A = S_{V_0} + S_{V_1} \cdot t + S_{V_2} \cdot t^2 + S_{V_3} \cdot t^3 + S_{V_4} \cdot t^4 \quad (\text{kg m}^{-3}) \quad (23)$$

$$\rho_A = S_{D_0} + S_{D_1} \cdot t + S_{D_2} \cdot t^2 + S_{D_3} \cdot t^3 \quad (\text{kg m}^{-3}) \quad (24)$$

Where t is the temperature in °C. Values of parameters S_{V_0} to S_{V_4} and S_{D_0} to S_{D_3} are listed in Table A1. The diffusion coefficients of gases in air (D_A) are calculated according to Fuller et al. (1966):

$$D_A = 0.001 \times T^{1.75} \cdot \frac{M_r^{0.5}}{[(P \cdot V_A^{1/3}) + V_b^{1/3}]^2} \quad (25)$$

Where P is the pressure in atm (assumed to be unity for all calculations presented in this work), V_A is the molar volume of air (assumed here to be $20.1 \text{ cm}^3 \text{ mol}^{-1}$) (Tucker and Nelken, 1990). M_r is a function of the relative molecular masses of air (M_A), assumed to be 28.97 (Tucker and Nelken, 1990), and of the gas of interest (M_b):

$$M_r = \frac{M_A + M_b}{M_A \cdot M_b} \quad (26)$$

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Air-water gas transfer velocity scheme

M. T. Johnson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Note that this method is defined by Fuller et al. (1966) as being applicable only to pairs of insoluble gases, but it has been successfully applied to the case of insoluble gases in air by Tucker and Nelken (1990). In a study of binary soluble gas pairs it performed less well than other more complex parameterisations, consistently overestimating diffusion by approximately 23% (Nain and Ferron, 1972). However, as k_a is proportional to $\frac{1}{D_A}^{2/3}$, such error (which is likely to be substantially smaller for a polar gas in mostly non-polar air) has only a small effect on the calculated k_a , so it is recommended here that it is applied irrespective of gas solubility. It is worth noting that the diffusion coefficients predicted using this method vary by up to an order of magnitude e.g. $D_A(\text{H}_2) \approx 0.5 \text{ cm}^2 \text{ s}^{-1}$, $D_A(\text{CH}_3\text{I}) \approx 0.06 \text{ cm}^2 \text{ s}^{-1}$, so it is important to apply a gas-specific D_A value in the calculation of k_a (note, however, that the difference between the D_A values for CO_2 and NH_3 is $\approx 40\%$ and this leads to a modest difference in k_a in Fig. 5).

3.3 Liquid phase transfer velocity, k_w

The liquid phase transfer velocity is calculated here according to Nightingale et al. (2000) (Eq. 27). This parameterisation is selected because i) it is a reliable measurement of in-situ gas exchange using a “purposeful dual tracer” approach (Asher, 2009); ii) it sits roughly in the middle of the other most commonly cited parameterisations of k_w , those of Wanninkhof (1992) and Liss and Merlivat (1986) and iii) it is in very good agreement with the updated bomb ^{14}C -derived global estimate of k_w - u relationship presented by Sweeney et al. (2007). There is considerable uncertainty (at least a factor of two) associated with the differences between different parameterisations of k_w . Asher (2009) suggests that up to 50% of the variability between different tracer and wind tunnel studies can be attributed to experimental uncertainty, supporting the approach of taking the middle of the three commonly used k_a parameterisations.

$$k_w = (0.222 \cdot u_{10}^2 + 0.333 \cdot u_{10}) \cdot \left(\frac{S_{\text{C}_w}}{S_{\text{C}_{600}}} \right)^{-0.5} \quad (27)$$

Air-water gas transfer velocity scheme

M. T. Johnson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Where $S_{c_{600}}$ is a Schmidt number value of 600, which is the typically quoted Schmidt number of CO_2 at 20°C in freshwater, to which the Schmidt number of the gas of interest under conditions of interest (S_{c_w}) is scaled. Note that Schmidt numbers are very temperature-dependent, so application of this scaling factor is important even for CO_2 . S_{c_w} is calculated according to Eq. (28):

$$S_{c_w} = \frac{\nu_w}{D_w} = \frac{\eta_w}{\rho_w \cdot D_w} \quad (28)$$

Where ν_w is the kinematic viscosity of water, D_w is the diffusivity of the gas of interest in water, η_w is the dynamic viscosity of water and ρ_w is the density. The density of saline water, in kg m^{-3} , is calculated according to Millero and Poisson (1981), according to Eqs. (A1) to (A5) (in Appendix A).

3.3.1 Water viscosity and density

The dynamic viscosity of water, η_w (or η_s in the case of water of non-zero salinity) is calculated using the temperature- and salinity-dependent viscosity model/mixing rule scheme of Laliberte (2007a) (Eqs. 29 to 31), which requires the compositions of seawater expressed as mass fractions of component solutes, which are derived here from the standard seawater definition of Millero et al. (2008) (Table A2).

The mixing rule follows the form:

$$\ln(\eta_s) = w_w \cdot \ln(\eta_w) + \sum w_i \cdot \ln(\eta_i) \quad (29)$$

Where η_s is the dynamic viscosity of the mixed-solute solution in cP (centipoise; $1 cP = 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$), w_w is the mass fraction of water in the solution, η_w is the dynamic viscosity of pure water in cP . For each solute in the solution, w_i is the mass fraction and η_i is the dynamic viscosity attributable to the particular solute. Laliberte (2007a) provides a numerically efficient (and for this purpose sufficiently accurate) term

for the temperature-dependent dynamic viscosity of pure water (at atmospheric pressure):

$$\eta_w = t + \frac{246}{0.05594 t^2 + 5.2842 t + 137.37} \quad (30)$$

where t is the temperature in °C. The dynamic viscosity of each component solute, η_i is calculated according to Eq. (31):

$$\ln(\eta_i) = \frac{v_1 \cdot (1 - w_w)^{v_2} + v_3}{(v_4 \cdot t + 1) \cdot \ln[v_5(1 - w_w)^{v_6} + 1]} \quad (31)$$

where v_1 to v_6 are experimentally-derived empirical constants for each solute. For the common solutes in seawater, values are provided by Laliberte (2007a). Note that Eq. (31) is corrected from the original paper according to Laliberte (2007b). Using the ionic composition of standard seawater (Millero et al., 2008) and pairing ions into the common salt constituents found in seawater (Table A2), a temperature- and salinity-dependent viscosity for seawater can then be calculated. This compares well to the fixed-salinity formulation for seawater viscosity of R. C. Hardy (ITTC, 2006) (Table 2).

3.3.2 Diffusion coefficients of gases in water

Diffusivity of a solute in a liquid solvent can be calculated by a number of methods. Using the tabulated data on measured vs calculated values of diffusivities given by Poling et al. (2001), it can be seen that for the mostly low molecular weight compounds of interest here, and when water is the solvent, the methods of Wilke and Chang (1955) (Eq. 32), Hayduk and Minhas (1982) (Eqs. 33 and 34) and Tyn and Calus (1975) perform best. The method of Tyn and Calus (1975), whilst likely to be the most accurate in the majority of cases (Poling et al., 2001), requires parachor data which is not available for many trace gases so only the other two methods are considered further.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



The method of Wilke and Chang (1955) gives diffusion coefficients in units of $\text{cm}^2 \text{s}^{-1}$:

$$D_{\text{WC}} = \frac{7.4 \times 10^{-8} T \cdot \sqrt{\Phi \cdot M_s}}{\eta_s \cdot V_b^{0.6}} \quad (32)$$

Where T is the temperature in Kelvin, M_s is the relative molecular mass of the solvent (18.01 in the case of water), η_s is the dynamic viscosity of the solvent in cP , Φ is the association factor of the solvent (2.6 for water) and V_b is the liquid molar volume of the gas of interest at its normal boiling point (in $\text{cm}^3 \text{mol}^{-1}$).

Hayduk and Minhas (1982) present a similar relationship, also in $\text{cm}^2 \text{s}^{-1}$:

$$D_{\text{HM}} = 1.25 \times 10^{-8} T^{1.52} \cdot \eta_s^{\varepsilon^*} \cdot (V_b^{-0.19} - 0.292) \quad (33)$$

and

$$\varepsilon^* = \frac{9.58}{V_b} - 1.12 \quad (34)$$

The Wilke and Chang (1955) and Hayduk and Minhas (1982) methods are then used to calculate a mean diffusivity for use in Eq. (28).

3.3.3 Liquid molar volume at boiling point (V_b)

Both of the above methods require the liquid molar volumes (V_b) of the solutes of interest. These can most effectively be calculated from the additive “Schroeder” method (Partington, 1949) (Table 3). This method is generally in good agreement with experimentally-derived values of V_b (Poling et al., 2001), but where experimentally-derived values are available for a particular compound it is recommended here that these should be used in preference.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



4 Comparison/validation

The new scheme presented here could be validated against directly measured trace gas fluxes from micrometeorological studies where concentrations of the gas of interest were also measured in the atmosphere and ocean, and one such analysis is conducted below. However, this is validating both the scheme and the underlying thin-film model of gas exchange, which is not the aim of this paper. Therefore the scheme is also used to recalculate transfer velocities and fluxes from two previous studies who also apply the thin-film model to approach problems of trace gas exchange.

4.1 CO₂ transfer velocity

The scheme presented in this work for calculating the liquid-phase transfer velocity is compared with the NOAA COARE algorithm (Fairall et al., 1996, 2003) applied to CO₂, as compared with directly measured fluxes by Hare et al. (2004). Figure 6 reproduces the measured and modelled CO₂ transfer velocities presented by Hare et al. (2004) along with transfer velocities for CO₂ calculated using the scheme presented here at $t=20^{\circ}\text{C}$, the temperature also used by Hare et al. (2004) for their calculations. Also included in the plot is the Nightingale k_w parameterisation, normalised to a Schmidt number of 660 (the commonly quoted value for CO₂ in seawater at 20 °C).

There are clear differences between the NOAA COARE algorithm and the scheme presented in this work, but this is to be expected because the COARE algorithm quantifies transfer velocity based on substantially more complex meteorological parameterisations. Furthermore, as this is an attempt to make a standardised approximation to the gas exchange velocity applying the approach of the thin film model, one would not expect the scheme to agree perfectly with measured or more complex modelled data, as not all factors are accounted for (e.g. bubble-mediated transfer, thermal instability). It is worth noting that the NOAA COARE algorithm was tuned to fit the GAS-EX data specifically, which explains the very strong agreement between measured and modelled transfer velocities. Considering this, both the scheme presented here and the

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Nightingale et al. (2000) term for k_w (the only difference between the two being the value of S_{c_A} applied), perform remarkably well compared to the COARE algorithm.

4.2 More soluble (gas-phase controlled) gas exchange

We use the scheme to calculate salinity-dependent Henry's law concentrations and transfer velocities for ammonia, and along with measured concentration gradients calculate and compare the gas-phase controlled flux of ammonia with that calculated by (Johnson et al., 2008). The results of this analysis are presented in Fig. 7. The main differences between the scheme presented here and that used by Johnson et al. (2008) are that the latter uses i) the molecular-weight dependent Duce et al. (1991) parameterisation of k_a and ii) a fixed 20% decrease in Henry's law solubility applied to account for the salting out effect.

Note that whilst there is normally good agreement between the methods, there are occasionally up to 25% differences between them (which are associated with high wind speeds and consequent larger fluxes from the new k_a parameterisation). There is a systematic bias in the data plotted in Fig. 7 to being above the one-to-one line, which in the negative region of the graph represents greater downward fluxes from the new scheme and in the positive region, smaller upward fluxes. This is due to the salinity correction applied in the new scheme being (at $S = 35$) approximately an 8% decrease in solubility, compared to the 20% applied by Johnson et al. (2008).

4.3 Gases of intermediate solubility

Finally, the relative contribution of the gas phase and liquid phase transfer velocities (k_a and k_w respectively) to the total transfer velocity is investigated. The contribution from both sides of the interface to total transfer has been identified as being of importance for gases of intermediate solubility (Liss and Slater, 1974; Archer et al., 2007). Archer et al. (2007) present data on the percentage reduction in the total transfer velocity (K_w) as a result of including both k_a and k_w in their calculations of fluxes from a marine time-

Air-water gas transfer velocity scheme

M. T. Johnson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



series of iodine-containing halocarbons, compared to calculation with k_w alone. The scheme presented here is used to reproduce these data (Table 4), assuming temperature, wind speed and salinity based on plots of environmental variables in Archer et al. (2007). Agreement is generally very good, which is positive validation for the scheme presented here, particularly considering that Archer et al. (2007) use experimentally determined diffusivities for the gases in question whereas those calculated here are derived from molecular structure.

5 Conclusions

Presented above is a numerical scheme for calculating the temperature- and salinity-dependent transfer velocity (and component parameters) of any gas across an air-water interface given basic physical chemistry data for the gas (relative molecular mass, K_H , $-\Delta_{\text{soln}}H/R$), component elements and molecular structure, the ionic composition of the medium and temperature, salinity and wind speed. A fully-implemented version of the scheme is provided in the Supplementary Material (see <http://www.ocean-sci-discuss.net/7/251/2010/osd-7-251-2010-supplement.zip>), along with input files for the composition of seawater and a file containing input data for 80 gases of potential interest to workers in the field of trace gas exchange.

The scheme is shown to agree well with previous methods of calculating k_a and k_w , although improvements have been made to the theoretically-determined gas-phase transfer velocity, k_a , and a novel approach to determining the salting out coefficients which are used to modify the Henry's law coefficients with salinity. Like most field-based studies of trace gas fluxes calculated from concentration measurements, this scheme does not currently account for processes such as bubble-mediated transfer, chemical enhancement, or microlayer effects, which should be applied to calculated fluxes on a case-by-case basis.

It is suggested that this scheme should be adopted by workers in the field who use the thin film model of trace gas exchange to calculate fluxes from their mea-

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



sured data to become a standard and intercomparable method. Whilst more complex micrometeorologically-based schemes exist e.g. NOAA COARE (Fairall et al., 1996, 2003) MESSY AIR-SEA (Pozzer et al., 2006), these are considerably more difficult to apply to a wide range of gases and the increased accuracy is probably not of great significance relative to the uncertainties in measured/estimated concentration gradients to which these schemes might be applied for gases other than those which are most intensively studied e.g. CO₂, CH₄, N₂O.

Appendix A

Further calculation details

A1 Air viscosity and density parameters

The temperature-dependent dynamic viscosity and density of saturated air is calculated using the methods of Tsilingiris (2008), using Eqs. (23) and (24). Values of the parameters used in these equations are given in Table A1.

A2 Water viscosity and density parameters and calculation

The density of water is calculated according to Millero and Poisson (1981) using Eqs. (A1) to (A5).

$$\rho_s = \rho_0 + A \cdot S + B \cdot S^{3/2} + C \cdot S \quad (\text{A1})$$

where ρ_s is the density at salinity, S ; ρ_0 is the density of pure water (Eq. A2) and parameters A , B and C are calculated according to Eqs. (A3) to (A5).

$$\rho_0 = 999.842594 + 0.06793952 \cdot t - 0.00909529 \cdot t^2 + 0.0001001685 \cdot t^3 - 0.000001120083 \cdot t^4 + 0.000000006536332 \cdot t^5 \quad (\text{A2})$$

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



where t is the temperature in °C

$$A = 0.824493 - 0.0040899 \cdot t + 0.000076438 \cdot t^2 - 0.00000082467 \cdot t^3 + 0.000000053875 \cdot t^4 \quad (\text{A3})$$

$$B = -0.00572466 + 0.00010277 \cdot t - 0.0000016546 \cdot t^2 \quad (\text{A4})$$

$$C = 0.00048314 \quad (\text{A5})$$

The viscosity parameters for Eq. (31) must be applied for each solute in the medium. These parameters are listed in Table A2, along with solute mass fraction (as a proportion of total salinity) derived from the ionic composition of standard seawater presented by Millero et al. (2008).

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Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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M. T. Johnson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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OSD

7, 251–290, 2010

Air-water gas transfer velocity scheme

M. T. Johnson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Air-water gas transfer
velocity scheme**

M. T. Johnson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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**Air-water gas transfer
velocity scheme**M. T. Johnson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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OSD

7, 251–290, 2010

Air-water gas transfer velocity scheme

M. T. Johnson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Table 1. $K_H/K_{H,0}$ (salting out factor) for gases measured in natural or synthetic seawater at salinity between 35 and 36 (except where otherwise stated), compared to values predicted by Eqs. (7) to (9).

Compound	K_H°	$K_H/K_{H,0}$ measured*	Reference	$K_H/K_{H,0}$ predicted
SF ₆	1.70×10^2	1.38 (31) ^a	Bullister et al. (2002)	1.36
Ne	9.09×10^1	1.21 (25)	Hamme and Emerson (2004)	1.21
N ₂	6.50×10^1	1.27 (25)	Hamme and Emerson (2004)	1.25
O ₂	3.15×10^1	1.25 (25)	Hamme and Emerson (2004)	1.23
CH ₄	3.15×10^1	1.24 (25) ^b	Yamamoto et al. (1976)	1.27
Ar	2.92×10^1	1.25 (25)	Hamme and Emerson (2004)	1.24
Kr	1.67×10^1	1.25 (20)	Weiss and Kyser (1978)	1.26
ethene	8.52×10^0	1.26 (20)	Breitbarth et al. (2004)	1.27
N ₂ O	1.70×10^0	1.22 (20)	Weiss and Price (1980)	1.24
CCl ₄	1.36×10^0	1.36 (20)	Bullister and Wisegarver (1998)	1.32
CCl ₄	1.36×10^0	1.27 (18.2)	Dewulf et al. (1995)	1.32
CO ₂	1.17×10^0	1.20 (25)	Teng and Yamasaki (1998)	1.24
CH ₃ Cl	3.72×10^{-1}	1.06 (22) ^x	Elliott and Rowland (1993)	1.25
toluene	2.73×10^{-1}	1.36 (18.2)	Dewulf et al. (1995)	1.30
CH ₃ Br	2.56×10^{-1}	1.22 (18)	De Bruyn and Saltzman (1997)	1.25
CH ₃ Br	2.56×10^{-1}	1.14 (22) ^x	Elliott and Rowland (1993)	1.25
CH ₃ I	2.15×10^{-1}	1.22 (22) ^x	Elliott and Rowland (1993)	1.26
benzene	2.05×10^{-1}	1.35 (18.2)	Dewulf et al. (1995)	1.30
CHCl ₃	1.36×10^{-1}	1.25 (18.2)	Dewulf et al. (1995)	1.27
DMS	8.18×10^{-2}	1.23 (18)	Wong and Wang (1997)	1.25

Air-water gas transfer velocity scheme

M. T. Johnson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Table 1. Continued.

Compound	K_H^\ominus	$K_H/K_{H,0}$ measured*	Reference	$K_H/K_{H,0}$ predicted
1-propylnitrate	4.09×10^{-2}	1.35 (5)	Kames and Schurath (1992)	1.25
ethylnitrate	2.56×10^{-2}	1.27 (5)	Kames and Schurath (1992)	1.23
methylnitrate	2.05×10^{-2}	1.20 (5)	Kames and Schurath (1992)	1.20
PPN	1.41×10^{-2}	1.16 (20) ^c	Kames and Schurath (1995)	1.22
PAN	9.98×10^{-3}	1.14 (20) ^c	Kames and Schurath (1995) 1	1.19
propanal	3.15×10^{-3}	1.22 (25)	Zhou and Mopper (1990)	1.16
ethanal	2.92×10^{-3}	1.14 (25)	Zhou and Mopper (1990)	1.15
ethanal	2.92×10^{-3}	1.14 (30)	Benkelberg et al. (1995)	1.15
acetone	1.36×10^{-3}	1.13 (25)	Zhou and Mopper (1990)	1.14
acetone	1.36×10^{-3}	1.12 (0 to 30) ^d	Benkelberg et al. (1995)	1.14
acetonitrile	8.18×10^{-4}	1.14 (20)	Benkelberg et al. (1995)	1.11
NH ₃	6.82×10^{-4}	0.93 (40) ^{x,e}	Sing et al. (1999)	1.08
methanal	1.36×10^{-5}	0.92 (25)	Zhou and Mopper (1990)	0.93
H ₂ O ₂	4.55×10^{-6}	0.83 (18)	Bandstra (2000)	0.84

Notes: * – measurement temperature given in parentheses; x – denotes data *not* used to derive Eq. (9); a – $S = 39$; b – $S = 34$, 0.6 °C difference between fresh and saltwater measurements; c – synthetic seawater; d – mean of 0, 15 and 30 °C measurements; e – measurement in $S \approx 400$ at 40 °C.

Air-water gas transfer velocity scheme

M. T. Johnson

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Air-water gas transfer velocity scheme

M. T. Johnson

Table 2. Comparison of the Laliberte (2007a,b) method for calculating the dynamic viscosity of multiple-solute solutions applied to seawater at $S = 35$ with the experimentally-derived method of R.C. Hardy (ITTC, 2006) (only valid at $S = 35$). All viscosities in $\text{kg m}^{-1} \text{s}^{-1}$.

Temperature/ $^{\circ}\text{C}$	η_s [Laliberté]	η_s [Hardy]	% difference
–5	2.265	2.244	0.934
0	1.897	1.880	0.914
5	1.614	1.605	0.583
10	1.392	1.390	0.136
15	1.215	1.219	–0.325
20	1.072	1.080	–1.750
25	0.954	0.965	–1.111
30	0.856	0.870	–1.398
35	0.773	0.786	–1.607

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Air-water gas transfer velocity scheme

M. T. Johnson

Table 3. Schroeder additive method for calculating V_b . For all atoms/structural items a molecule contains, the sum of the increments will give the molar volume. E.g. $\text{CH}_2=\text{CH}_2$ contains 2 carbon atoms, 4 hydrogen atoms and 1 double bond so the Schroeder V_b is $2 \times 7 + 4 \times 7 + 7 = 49 \text{ cm}^3 \text{ mol}^{-1}$. * Applies to all kinds of cyclic features and is applied only once to ring-containing compounds irrespective of the number of rings present.

Atom/feature	Increment/ $\text{cm}^3 \text{ mol}^{-1}$
Carbon	7.0
Hydrogen	7.0
Oxygen	7.0
Nitrogen	7.0
Bromine	31.5
Chlorine	24.5
Fluorine	10.5
Iodine	38.5
Sulfur	21.0
Ring*	-7.0
Double bond	7.0
Triple bond	14.0

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Air-water gas transfer velocity scheme

M. T. Johnson

Table 4. Comparison of the reduction in calculated total transfer velocity (K_w) for a series of iodocarbons from the dataset of Archer et al. (2007) when considering both k_w and k_a , relative to the transfer velocity calculated using k_w alone.

Compound	% reduction, Archer et al. (2007)	% reduction, this work
CH ₃ I	3	2.3
C ₂ H ₅ I	2	2.1
CH ₂ ICl	14	11
CH ₂ IBr	23	21
CH ₂ I ₂	32	33

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Air-water gas transfer
velocity scheme

M. T. Johnson

Table A1. Parameters for calculating the dynamic viscosity (η_A) and density (ρ_A) of saturated air according to Tsilingiris (2008). These values are for substitution into Eqs. (23) and (24).

η_A parameter	value	ρ_A parameter	value
S_{V_0}	$1.715747771 \times 10^{-5}$	S_{D_0}	1.293393662
S_{V_1}	$4.722402075 \times 10^{-8}$	S_{D_1}	$-5.538444326 \times 10^{-3}$
S_{V_2}	$-3.663027156 \times 10^{-10}$	S_{D_2}	$3.860201577 \times 10^{-5}$
S_{V_3}	$1.873236686 \times 10^{-12}$	S_{D_3}	$-5.2536065 \times 10^{-7}$
S_{V_4}	$-8.050218737 \times 10^{-14}$	–	–

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

I◀

▶I

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Air-water gas transfer velocity scheme

M. T. Johnson

Table A2. Parameters for calculating solute viscosity in water, and mass fraction of each solute (as a proportion of total salinity) for Eqs. (29) and (31).

Compound	mass fraction	v_1	v_2	v_3	v_4	v_5	v_6
NaCl	0.798	16.22	1.3229	1.4849	0.0074691	30.78	2.0583
KCl	0.022	6.4883	1.3175	-0.7785	0.09272	-1.3	2.0811
CaCl ₂	0.033	32.028	0.78792	-1.1495	0.0026995	780860	5.8442
MgCl ₂	0.047	24.032	2.2694	3.7108	0.021853	-1.1236	0.14474
MgSO ₄	0.100	72.269	2.2238	6.6037	0.0079004	3340.1	6.1304

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Air-water gas transfer velocity scheme

M. T. Johnson

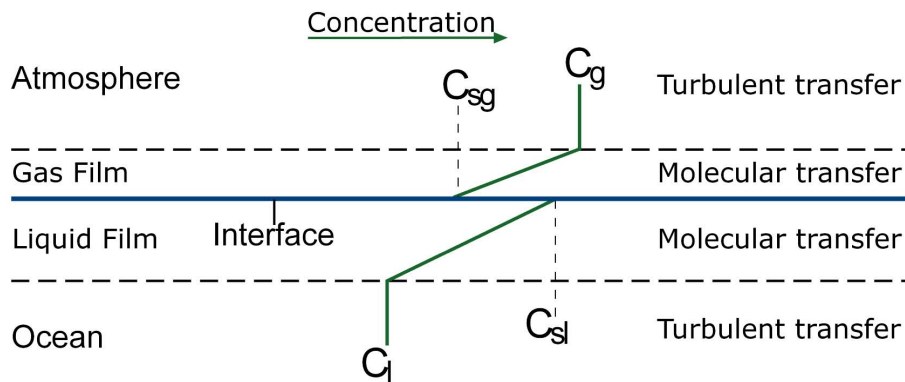


Fig. 1. Schematic of the thin film model of air-sea gas exchange after Liss and Slater (1974).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Air-water gas transfer velocity scheme

M. T. Johnson

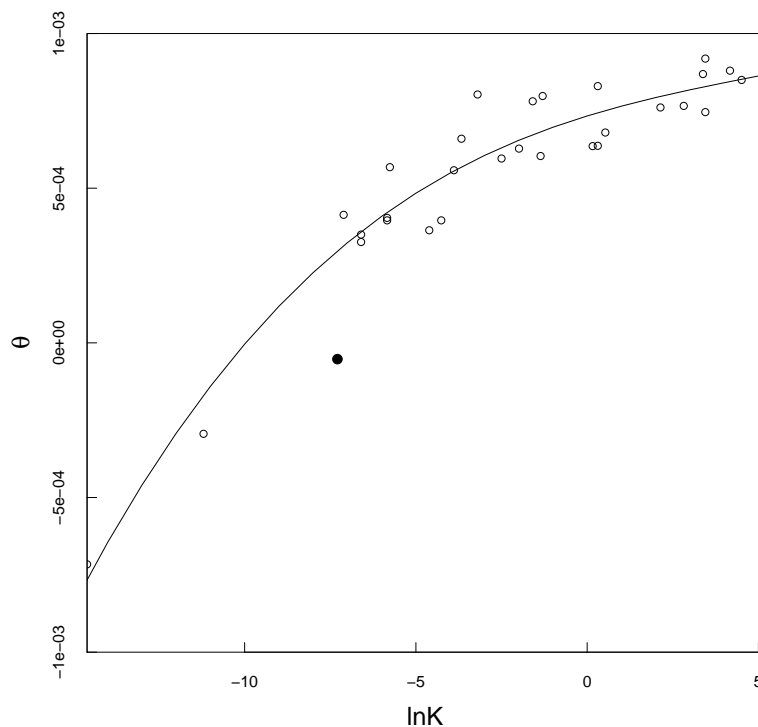


Fig. 2. Regression of the natural logarithm of the Henry's law constant at $S = 0$ and $T = 25\text{ }^{\circ}\text{C}$ with the molar volume scaling factor, θ for the gases listed in Table 1, with the exception of the data of Sing et al. (1999) (marked as solid point on chart) and that of Elliott and Rowland (1993) (not shown – see main text for details).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

I◀

▶I

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Air-water gas transfer velocity scheme

M. T. Johnson

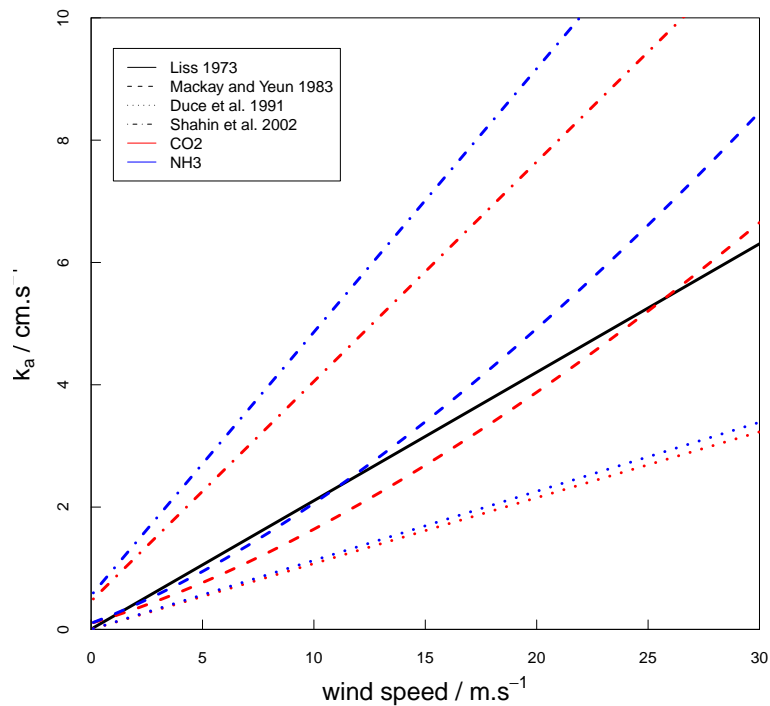


Fig. 3. Comparison of different parameterisations of k_a , the gas phase transfer velocity (Eqs. 10 to 13) for CO_2 and NH_3 , calculated at 15°C , where applicable. Note that the parameterisation of Liss (1973) (black line), is not gas-specific.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Air-water gas transfer velocity scheme

M. T. Johnson

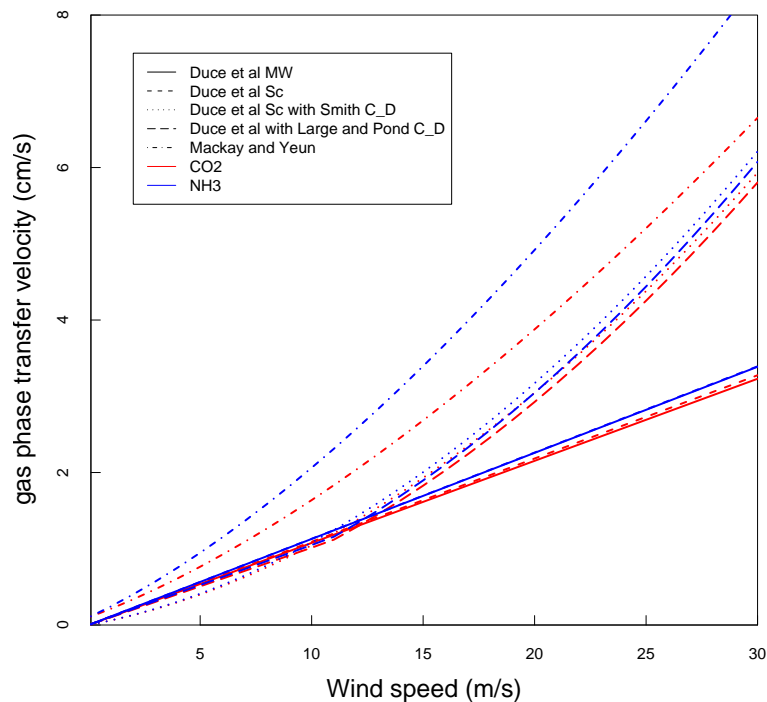


Fig. 4. Comparison of Duce et al. (1991) k_a applying 3 different parameterisations of C_D with the k_a parameterisation of Mackay and Yeun (1983), for NH_3 and CO_2 . Duce et al MW is the molecular-weight based derivation of k_a presented by Duce et al. (1991) (Eq. 10). Duce et al Sc corresponds to Eq. (17) with $C_D=1.3\times 10^{-3}$.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Air-water gas transfer velocity scheme

M. T. Johnson

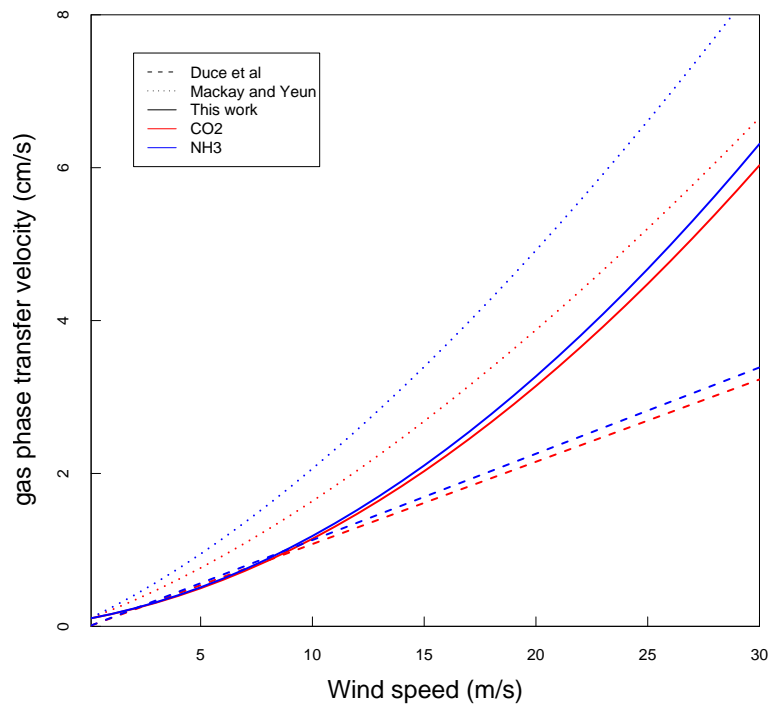


Fig. 5. Comparison of the k_a schemes of Duce et al. (1991), Mackay and Yeun (1983) and this work (Eqs. 19 and 20), for NH_3 and CO_2 .

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Air-water gas transfer velocity scheme

M. T. Johnson

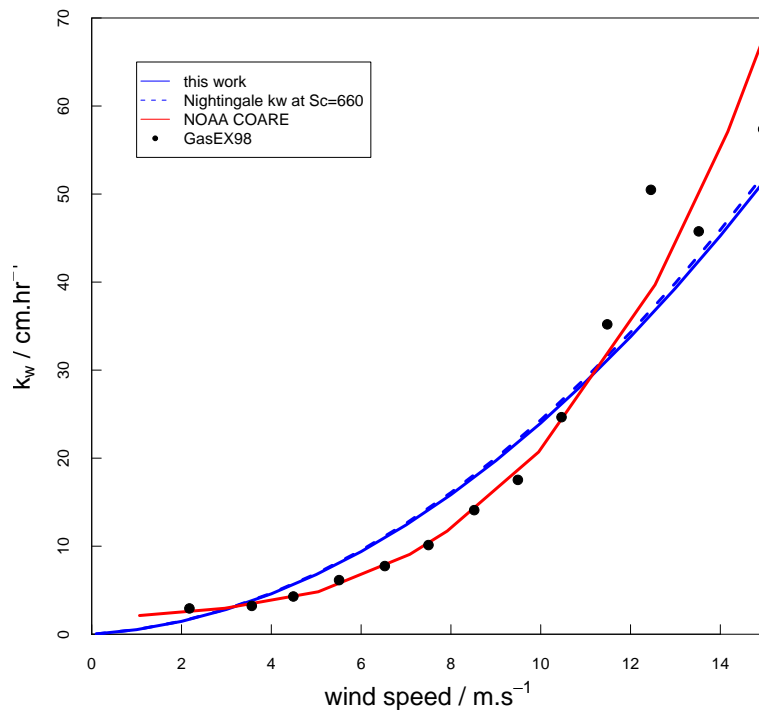


Fig. 6. Comparison of the NOAA COARE algorithm tuned to directly-measured transfer velocities from the GAS-EX98 experiment (Hare et al., 2004) with the scheme presented here, for a temperature of 20°C . Also shown is the Nightingale et al. (2000) parameterisation fixed at a Schmidt number of 660.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

**Air-water gas transfer
velocity scheme**

M. T. Johnson

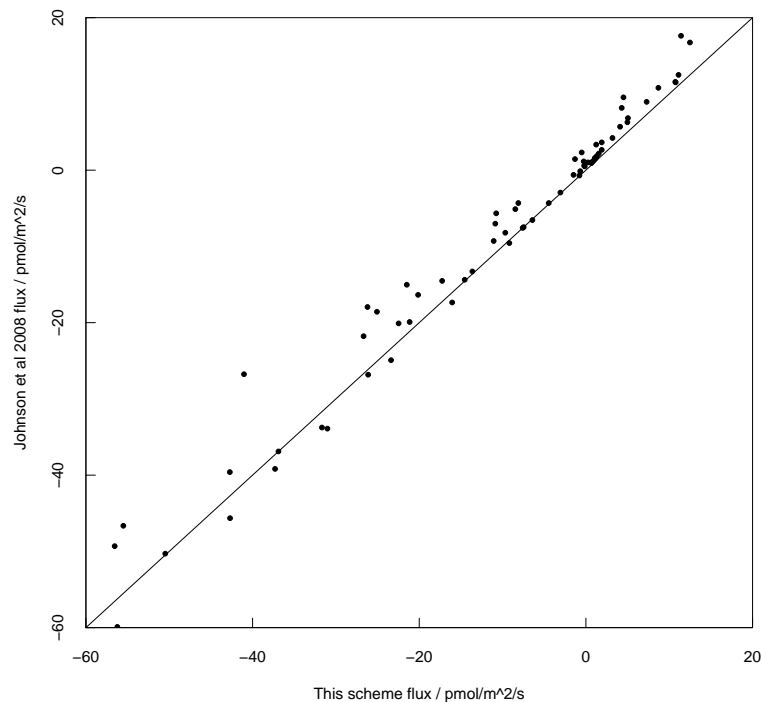


Fig. 7. Comparison of the NH_3 ocean-atmosphere fluxes from measured data as calculated by Johnson et al. (2008) and using the scheme presented in this work.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[I◀](#)[▶I](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)