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Models for air–water gas transfer: an experimental investigation

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ABSTRACT

The air–water transfer velocities for H_2, He and Xe have been measured simultaneously in laboratory-tank experiments. Using average values from the existing literature data for the molecular diffusivities of the gases, the transfer velocities are found to vary with the diffusivity raised to the power 0.57. This exponent is in reasonable agreement with the findings from other laboratories, as well as field studies, provided average diffusivities are used consistently. Although interpretation is limited by uncertainties in presently available diffusion coefficients, the results may be interpreted as supportive of both the surface-renewal and boundary-layer models of air–water gas exchange, but they provide little evidence for the appropriateness of the film model.

1. Introduction

The air–water transfer of gases which are sparingly soluble in water and do not react rapidly in the aqueous phase is controlled by processes in the near-surface water (Liss, 1973). Gases for which this applies include O_2, CO_2, the inert gases, CO, CH_4, CH_3I, $(CH_3)_2S$, freons and other low molecular weight halocarbons. Various models have been proposed to describe the exchange of gases of this type across air–water interfaces in the natural environment. Several of these have their origins in chemical engineering studies, but more recently approaches from atmospheric boundary-layer theory have been employed. In this latter case, the model was originally developed for transfer of gases for which aerodynamic processes were dominant (e.g. H_2O, SO_2, NH_3), and has been translated so as to apply to gases for which hydrodynamic mechanisms are the controlling factors.

The simplest approach, and probably the one most widely applied, is the film model developed by Whitman (1923) for chemical engineering systems. In it, the main body of the fluid (liquid or gaseous) is assumed to be well mixed, the rate of interfacial transfer being determined by molecular diffusion of the gas molecules across a stagnant layer (or film) of fluid (thickness z) adjacent to the surface. In this model, the rate of gas exchange, expressed in terms of a transfer velocity k_x (defined as the flux of gas 'x' per unit of concentration gradient driving its interfacial exchange), is given by

$$k_x = \frac{D_x}{z}, \tag{1}$$

where D_x is the coefficient of molecular diffusion of the gas. From (1), it is clear that k_x is proportional to D_x to the power one.

Although molecular processes will become progressively more important as the interface is approached, the existence of a stagnant film whose thickness, for a given turbulence, is invariant with time and space, seems physically unrealistic. This led Higbie (1935) and later Danckwerts (1951) and Dobbins (1956) to develop a variety of surface renewal models in which the stagnant fluid close to the interface is replaced periodically by material from the bulk. The physical process (and its mathematical description) by which liquid is

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envisaged as being transferred from bulk to near-surface is somewhat different in each of these versions of the surface renewal model. However, for present purposes, the important point is that all of the variants predict that the transfer velocity will be proportional to the coefficient of molecular diffusion to the power 0.5. Similarly, the so-called large and small eddy models of Fortescue and Pearson (1967), and Lamont and Scott (1970), respectively (in which transfer in the near-surface water is described in terms of a series of cells of rotating fluid), also lead to the prediction that $k_x \propto D_x^{1/2}$.

Finally, Deacon (1977) has used boundary-layer theory developed in micrometeorology to predict gas transfer rates in near-surface water. By using Reichardt's (1951) formulation of the velocity profile in turbulent air flow over a smooth, rigid surface, and assuming conservation of shear stress across the air–water interface, Deacon obtains the following relationship.

$$k_x = 0.082 Sc_x^{-2/3} (\rho_a/\rho_w)^{1/2} u_* \qquad (2)$$

where Sc_x is the Schmidt number (ratio of kinematic viscosity to molecular diffusivity) in the water, ρ_a and ρ_w are the densities of air and water, respectively, and u_* is the friction velocity in the air. It is apparent that according to this model, k_x is proportional to $Sc_x^{-2/3}$ and therefore to $D_x^{2/3}$.

From the various models briefly reviewed above, it is clear that $k_x \propto D_x^n$, but the value of n is uncertain and can vary from 1 (film model), through $\frac{2}{3}$ (boundary-layer approach), to $\frac{1}{2}$ (surface-renewal models). Values of n even lower than 0.5 are conceivable, since in the limit of turbulence overwhelming molecular transfer, there will be no dependency of k_x on D_x, i.e. $n \to 0$ (Kishinevsky and Serebryansky, 1956).

Although there is a lively debate as to the relative merits of the different models, there have been rather few attempts to try to adjudicate between them by experiment. Here we present the result of one such exercise.

Since $k_x \propto D_x^n$ it follows that,

$$\frac{k_1}{k_2} \propto \left(\frac{D_1}{D_2}\right)^n \qquad (3)$$

or

$$\log\left(\frac{k_1}{k_2}\right) \propto n \log\left(\frac{D_1}{D_2}\right). \qquad (4)$$

Thus, by measuring k values simultaneously for two or more gases, and knowing their respective diffusivities, it is possible to solve (4) to derive a value of n applicable to the conditions of the experiment. By conducting a series of experiments covering a range of liquid stirring regimes, it may be possible to comment on the applicability of the various models under particular mixing conditions.

In this paper, we report the findings of a study conducted in a laboratory tank in which the air–water transfer velocities of H_2, He and Xe have been measured simultaneously. These gases were selected in part because of the large spread in diffusivity between Xe and the other two, which should maximize any differences between the corresponding transfer velocities, and thus aid in accurately deriving the value of n from (4). To avoid the complicating effects of temperature changes on k_x and D_x, all the experiments were carried out at a common water temperature of 12 °C. Several series of experiments were performed with different degrees of stirring of the water in the tank.

2. Measurement of air–water gas transfer

2.1. *Experimental procedure*

The experiments were conducted in a circular tank similar to that described by Mancy and Okun (1965). The diameter of the tank was 242 mm with a surface area of 460 cm^2. Four baffles of length 80 mm and height 43 mm were attached at right angles to the walls of the vessel. The water was mixed by a magnetic stirrer, using a follower of length 60 mm and diameter 10 mm. A stroboscope was used to maintain a constant stirring rate in each experimental run by adjusting the magnetic stirrer so that the stirring bar appeared motionless in the strobe light. All experiments were conducted at 12 ± 0.4 °C, with 4.0 l of distilled water.

To remove organic compounds from the trough, it was always filled with a weak hydrogen peroxide solution when not in use.

The experiments were begun by shaking a third of the water with each of the gases (He, H_2 and Xe). After pouring the solutions into the experimental tank, stirring was commenced.

Aliquots (5 ml) of the tank water were drawn into glass syringes at set time intervals. The time intervals were chosen for each stirring regime so

that 10 samples would span three half-exchange times for xenon (the gas with lowest transfer rate). The water samples were equilibrated with 2 ml of air at room temperature. The air in the syringe was then analysed using a Perkin–Elmer F 17 gas chromatograph, with a stainless steel column (5 m long, 3.18 mm i.d.) packed with a 60–70 mesh 5 Å molecular sieve at a constant oven temperature of 35 °C and a neon carrier gas flow of 40 cm^3 min^{-1}. The gases were determined using a thermal conductivity detector. This method of gas analysis was originally described by Karlsson (1966) and modified by Thouzeau (1976). The nitrogen peak from the air was used as internal standard. Peak areas were measured using a Hewlett–Packard 3390 A integrator.

The transfer velocity for each of the three gases was determined by linear regression analysis of the concentration (C) data on a plot of ln C against time (t),

$$\frac{V}{A}\ln(C_t - C^*) = \frac{V}{A}\ln(C_{t_0} - C^*) - k(t - t_0), \quad (5)$$

where C^* is the water concentration at equilibrium and is assumed to be equal to zero for the gases used here. V/A is the ratio of the volume of water in the tank to its surface area which, for the perpendicular-sided tank employed, is given by the water depth (8.70 cm). The experiments were repeated at least five times at each stirring speed, except for the set at 550 rpm where only three successful experiments were performed due to deterioration of the GC columns.

2.2. *Experimental results*

The results of all 34 experiments are shown in Fig. 1. Both transfer velocity (a) and ratio of transfer velocities (b) are shown as functions of stirrer speed.

3. Discussion

3.1. *Diffusion coefficients*

In order to interpret the experimental results in terms of (4), it is necessary to have appropriate values of the diffusion coefficients for the gases of interest. However, determination of diffusion coefficients of sparingly soluble gases in water seems to be a difficult measurement to perform accurately. For He and especially Xe, there are very few determinations of D, although the situation for H_2, O_2 and CO_2 (the last two will be referred to later) is rather better in this respect. In Fig. 2 all the measurements available to us for D in distilled water are plotted as a function of water temperature. It is clear that considerable variations exist between the different data sets.

Another approach to finding a correct ratio D_1/D_2 is to make use of the predictive equations

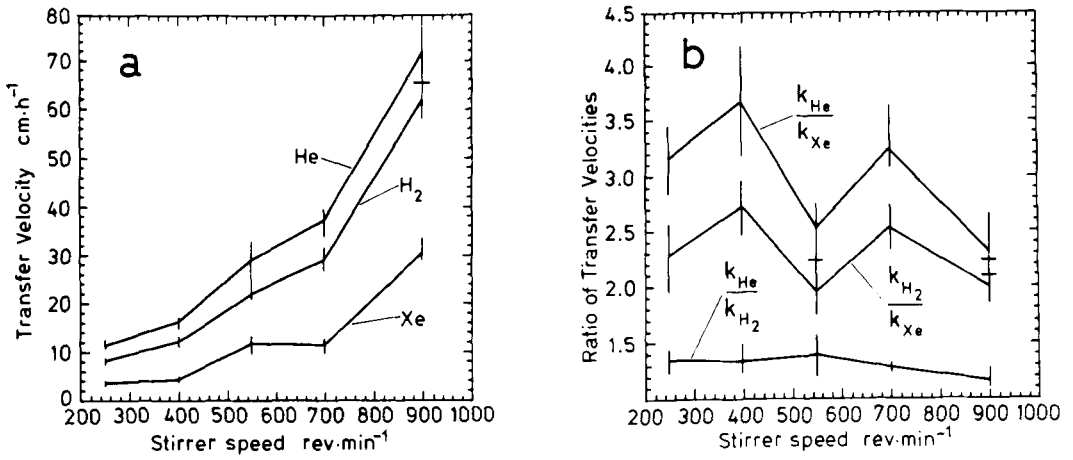

Fig. 1. Variation of (a) transfer velocities and (b) ratios of transfer velocities with stirrer speed. Vertical bars indicate the range of the values obtained in each set of experiments.

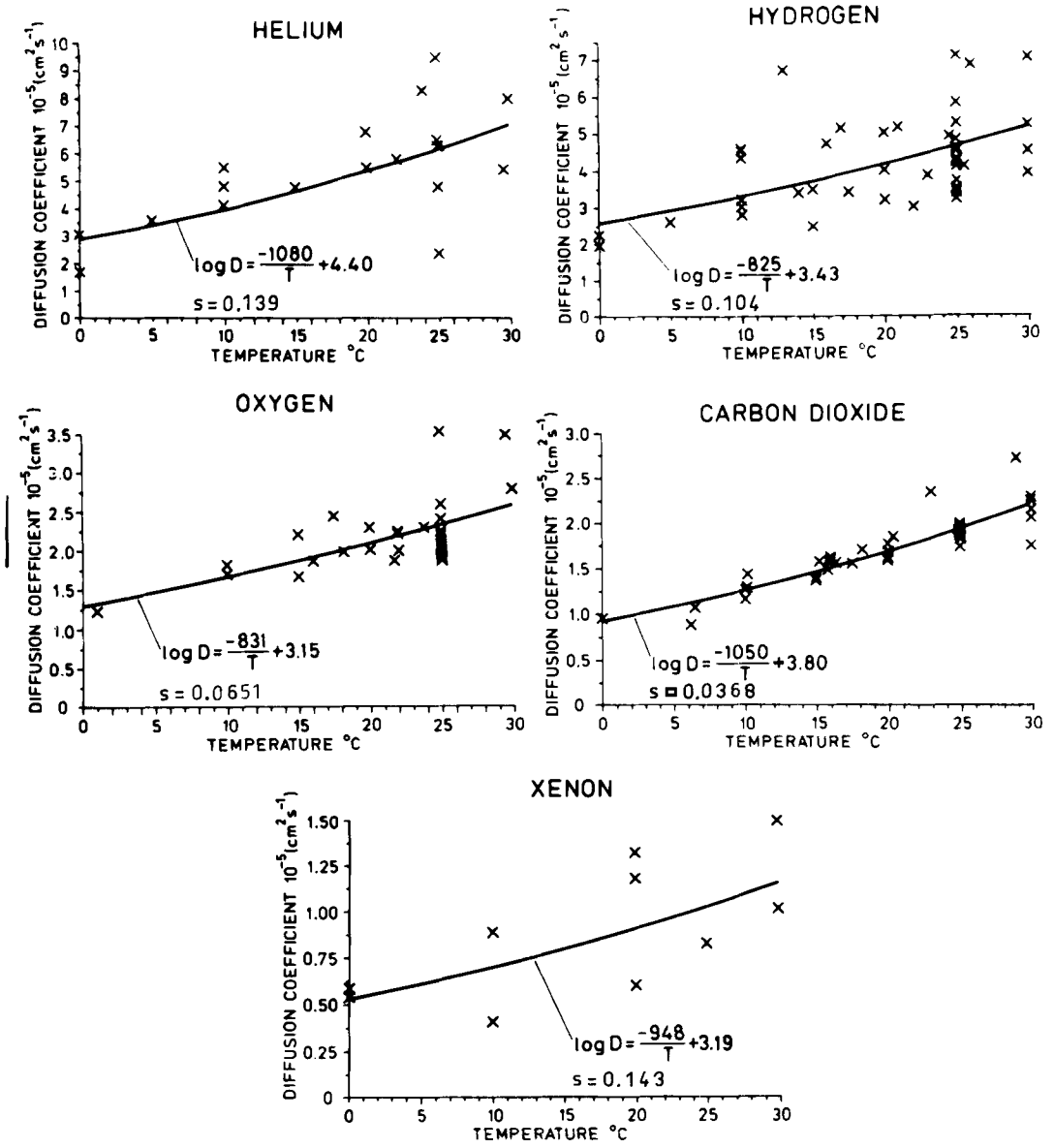

Fig. 2. The diffusion coefficients in water of He, H_2, O_2, CO_2, and Xe as a function of temperature. The available literature values are shown together with the best-fit curves of $\log D = A/T + B$. The standard deviation (s) of $\log D$ about the regression line is also shown. The data for the diffusion coefficients have been compiled from: Boerboom and Kleyn (1969); de Block and Fortuin (1981); Ferrell and Himmelblau (1967); Himmelblau (1964); Krieger et al. (1967); Mazarei and Sandall (1980); O'Brien and Hyslop (1977); Pollack (1981); St-Denis and Fell (1971); Tham et al. (1970); Unsworth and Gillespie (1971); Wise and Houghton (1966, 1968).

developed for diffusivities of dissolved substances in liquids. The oldest of these is the Stokes–Einstein equation (Einstein, 1905) relating the diffusivity of a solute to the frictional force on a sphere falling through a viscous medium. The Stokes–Einstein equation has two limiting cases with

$$D_{AB} = (kT/6\pi)\,\eta_B\,R_A \qquad (6)$$

for the situation when there is no tendency for the fluid to slide at the surface of the diffusing species (D_{AB} is the diffusivity of solute A in solvent B, k the Boltzmann constant. T the absolute temperature, η_B the viscosity, and R_A the radius of diffusing molecule). When the solvent is assumed to move freely at the surface of the solute, the diffusivity is given by

$$D_{AB} = (kT/4\pi)\,\eta_B\,R_A \tag{7}$$

Himmelblau (1964) suggests that the factor 4 in the denominator of (7) has to be replaced by a still smaller factor when the diffusing molecules are smaller than the solvent molecule, which is the case for diffusion of He and H_2 in water. Uncertainty over this factor, together with the disagreement between experimental results and the Stokes–Einstein law (Pollack, 1981), makes use of (6) and (7) unreliable when calculating the ratio of diffusion coefficients: this is particularly pronounced for the ratios of greatest interest in this paper (D_{He}/D_{Xe} and D_{H_2}/D_{Xe}).

Several empirical equations for predicting diffusivities have been suggested, of which the three most widespread are:

Othmer and Thaker (1953),

$$D_{AB} = C_1/(\eta_B^{1.1}\,V_A^{0.6}), \tag{8}$$

$$C_1 = 17.6\cdot 10^{-16}\ \mathrm{m^{2.7}\,kg^{1.1}\,mol^{-0.6}\,s^{-2.1}},$$

where V_A is the molar volume of A;

Scheibel (1954),

$$D_{AB} = C_2\,kT/(\eta_B\,V_A^{1/3}) \qquad \text{for } V_A < V_B \tag{9}$$

$$C_2 = 18.3\cdot 10^6\ \mathrm{mol^{-1/3}};$$

and Wilke and Chang (1955)

$$D_{AB} = C_3\,kT(2.26\cdot M_B)^{1/2}/\eta_B\,V_A^{0.6}), \tag{10}$$

$$C_3 = 42.6\cdot 10^5\ \mathrm{m^{0.8}\,kg^{-0.5}\,mol^{-0.1}},$$

where M_B is the molar mass of B. Common to all three approaches is the exclusion of the outstandingly large diffusivities of helium and hydrogen in the mathematical analysis used to determine the constants (Hayduk and Laudie, 1974). Although some recent work (de Block and Fortuin, 1981) supports the use of the Wilke-Chang equation for D_{H_2}, other workers (Mazarei and Sandall, 1980) report hydrogen diffusivity values with large deviations from the predicted values.

Because of the difficulties outlined in the use of theoretical and empirical equations to predict D, and in view of the uncertainty and bias which can arise in trying to discriminate between experimentally determined diffusivities, we have chosen to fit all the laboratory measurements of D for each gas to the relationship suggested by Himmelblau (1964),

$$\log D = \frac{A}{T} + B \tag{11}$$

and subsequently used the resulting average diffusivities obtained from the best-fit curves through the plotted points.

3.2. *Calculation of n and comparison with previous work*

Values of n calculated from our experimental results are shown in Table 1. Values derived from the He–H_2 pair are unreliable due to the small diffusivity differences for these two gases. For the He–Xe and H_2–Xe pairs, the range of calculated n is from 0.43 to 0.74, with a mean of 0.57. The value of $\bar{n} = 0.57$ is based on the average diffusion coefficients used to compute the individual values of n. Calculating the full range of n using the envelope of the range in the experimental results

Table 1. *Ratios of transfer velocities and corresponding values of n, as a function of stirrer speed*

Stirrer speed (r.p.m.)	$\frac{k_{He}}{k_{Xe}}$	n	$\frac{k_{H_2}}{k_{Xe}}$	n	$\frac{k_{He}}{k_{H_2}}$	n
250	3.16	0.66	2.28	0.53	1.35	1.5
400	3.67	0.74	2.73	0.65	1.34	1.5
550	2.53	0.53	1.95	0.43	1.38	1.6
700	3.24	0.67	2.53	0.60	1.28	1.2
900	2.32	0.48	2.00	0.45	1.16	0.75

$$n = \frac{\ln \frac{k_a}{k_b}}{\ln \frac{D_a}{D_b}}$$

From Fig. 2:
$D_{He} = 4.22\cdot 10^{-5}\ \mathrm{cm^2\,s^{-1}}$, at 12 °C
$D_{H_2} = 3.47\cdot 10^{-5}\ \mathrm{cm^2\,s^{-1}}$, at 12 °C
$D_{Xe} = 0.736\cdot 10^{-5}\ \mathrm{cm^2\,s^{-1}}$, at 12 °C
Average of the n values for He/Xe and H_2/Xe ($\bar{n}$) = 0.57.

and the standard deviation of the diffusion coefficients from the regression analysis of log D against T^{-1} yields: $0.26 \leqslant n \leqslant 1.28$. Although the range of n is large, 80% of the data points are within the interval $0.4 \leqslant n \leqslant 0.8$ with a median value of 0.57 and an average of 0.60. Clearly the greatest uncertainties in n arise from the wide range of the diffusion coefficient data (which come about because of systematic differences between the experimental procedures used to determine D values). In the light of these systematic differences, it is logical, when calculating the range of n, to consistently use maximum or minimum diffusion values for all gases. Maximum diffusion coefficient values give $\bar{n}_{max} = 0.59$, whereas minimum values give $\bar{n} = 0.57$.

The above values compare quite well with results from other laboratory studies. For example, Smith et al. (1980) compare transfer velocities for 12 gases, covering a wide range of diffusivities as well as chemical properties, and derive a mean n of 0.61 ± 0.07 (their Fig. 4).

From the data given in Metzger and Dobbins (1967) their Figs. 6 and 7, it is possible to calculate n for the gas pairs He/N_2 and He/O_2. Using values for D_{He} and D_{O_2} from our Fig. 2, and D_{N_2} from their Table I, a mean of 0.62 (range 0.58–0.68) can be computed. Ledwell (1982) has recently reported results from a wind tunnel study comparing the transfer velocities of He, N_2O and CH_4 and derives a value for $n = 0.47 \pm 0.14$.

3.3. *Calculation of n from experiments at different temperatures*

An alternative approach to the determination of n is to measure how k for any gas varies with temperature. The transfer processes in a transition regime between turbulent and molecular transfer are intrinsically controlled by the dimensionless ratio of the respective molecular transport constants for momentum (viscosity) and matter (diffusivity), i.e. the Schmidt number. Thus the diffusivity dependence exponent is given by:

$$\log \frac{k_1}{k_2} \propto n \log \frac{Sc_2}{Sc_1}, \qquad (12)$$

with k_1 and k_2, Sc_1 and Sc_2 referring to different temperatures. Since all the results presented in this paper were obtained at a fixed temperature (12 °C), they cannot be used in this context, and we have had to rely on data from papers in the literature. In order to treat these results in a consistent manner, diffusivity values from Fig. 2 of this paper have been used, except where indicated.

The results of Downing and Truesdale (1955) for k_{O_2} as a function of temperature (their Fig. 5 and Table 1) present a problem because the transfer velocities are linearly related to temperature, in contradiction to expectations from the Arrhenius relationship. However n values calculated for this data ($0.45 < n < 0.8$) compare quite well with those discussed above. Metzger and Dobbins (1967) give data for k_{He} and k_{N_2} over a range of temperatures (their Figs. 6 and 7), and values of n calculated from these data are in the range 0.2–0.6 for He and 0.1–0.5 for N_2 (using their value for D_{N_2}). As will be discussed later, there is some indication in their results of a consistent change in n with degree of water turbulence. Jähne et al. (1979) calculate $n = 0.4$ from a study of CO_2 exchange at 4 °C and 20 °C in a circular wind tunnel. Martinelli (1979) gives results of an experiment in which k for O_2 and CO_2 was measured in a laboratory tank over the temperature range of 10–40 °C. Although detailed, there is some uncertainty over these results, since the data do not appear to obey the Arrhenius relationship particularly well. Values of n calculated from this data set are ~0.3 for CO_2 and ~0.4 for O_2.

3.4. *Dependence of n on turbulence*

Since it has been suggested that the film and surface renewal models are more likely to apply to gas exchange under calm and rough conditions, respectively, it is of interest to see whether the results discussed here give any support to this idea. Our own data show only a weak change in n with degree of water stirring (Table 1). Fig. 1b does appear to exhibit some narrowing of the differences in k values between the various gases as the water becomes more turbulent. More pronounced changes in n are shown by the data of Metzger and Dobbins (1967), where from their Figs. 6 and 7 we calculate n to increase consistently with decrease in stirring. For example, for He, $n = 0.3$ at the highest degree of turbulence, rising to 0.6 at the lowest stirring rate. Kishinevsky and Serebryansky (1956) appear to find $n \sim 0$ in a series of experiments using H_2, N_2, and O_2 with very high water turbulence (stirrer speed 1700 rpm, which we calculate from

their results to correspond to a transfer velocity of approximately 1000 cm h^{-1}, which seems unrealistically large and certainly much higher than achieved in any of the other experiments discussed here).

3.5. *Determination of n from field results*

Recently Torgersen et al. (1982) have presented results for a field experiment to measure k_{Rn} and k_{He} for a freshwater lake. From the results, they calculate a value of $n = 1.22^{+>0.12}_{-0.35}$, which they interpret as "clearly supporting the stagnant film model". However, this conclusion is very much dependent on accurate diffusivity values for the two gases. Although we have no more information on the diffusivity of Rn than was available to Torgersen et al. (a single value of $1.14 \pm 0.07 \cdot 10^{-5}$ cm^2 s^{-1} at 18 °C determined by Róna (1917), it is arguably more reliable to obtain D_{Rn} from the best-fit line through the data in Fig. 2 for D_{Xe}, since D values for Rn and Xe are likely to be very close (their covalent radii differ by only 2%, Torgersen et al., 1982). The field results were obtained at a lake water temperature of about 19°, so that assuming D_{Rn} equal to $D_{Xe} = 0.88$, gives a D_{He}/D_{Rn} ratio of 5.9 (compared to the value of 3 with a range of 2.7 to 4.6 used by Torgersen et al., 1982). With $D_{He}/D_{Xe} = 5.9$, the field results for $k_{He}/k_{Rn} = 3.8$ yield a value of $n = 0.76$. This value is an upper limit for the field results, since D_{Rn} must be smaller than D_{Xe}. (Uncertainties in the diffusion coefficient as discussed above could give a range of $0.55 \leqslant n \leqslant 1.19$.)

4. Conclusions

Table 2 contains all the values given in the previous section for n, derived using different temperatures and gases and from the field results. Inspection of the table shows that our experimental mean value for n of 0.57 is in rather good agreement with most of the results from other studies. The value of $n = 0$ obtained by Kishinevsky and Serebryansky (1956) was obtained with such a turbulent system that it is not surprising that the exponent falls outside the range of all the other results. At the opposite extreme, the highest value of all ($n = 1.22$ as calculated by Torgersen et al., 1982) is probably too high, due to the use of inappropriate values for the gas diffusivities; our recomputation of their results yields $n = 0.76$, in much better agreement with the bulk of laboratory data.

Table 2. *Values of n from this and other work*

Authors	n	Note
This work	$0.57 \pm 0.15 \binom{+0.7}{-0.3}^*$	a
Smith at al. (1980)	0.61 ± 0.07	a
Metzger and Dobbins (1967)	0.62	a
Kishinevsky and Serebryansky (1956)	0	a
Ledwell (1982)	0.47 ± 0.14	a
Downing and Truesdale (1955)	0.45–0.8	b
Metzger and Dobbins (1967)	0.1–0.6	b
Jähne et al. (1979)	0.41	b
Martinelli (1979)	0.3–0.4	b
Torgersen et al. (1982)	$1.22 \binom{+>0.12}{-0.35}$	c
Torgersen et al. (1982)	$0.76 \binom{+0.43}{->0.21}^*$	c, d

Notes
a: n determined using $k_a/k_b \propto (D_a/D_b)^n$.
b: n determined from temperature dependence of k.
c: n determined from field results.
d: n recalculated in this work.
* The envelope of all errors is shown in parenthesis. For details see text.

It is readily apparent that the results of calculations for n utilizing two different gases are critically dependent on values chosen for the gas diffusivities. We have used a consistent procedure for obtaining diffusivities and this certainly leads to a narrowing of the ranges derived for n. As shown earlier, consistent use of maximum or minimum, rather than average, diffusivities would not significantly alter calculated values for the exponent. However, use of a maximum diffusivity for one gas and a minimum value for the other can clearly produce a much greater range in n. In view of the large uncertainties which exist over diffusivity values, it would seem more appropriate at present to use averages for D. There may be an argument for consistently using minimum D values, since this may indicate experimental results which are least affected by turbulent mixing (de Block and Fortuin, 1981), but this does not appear to significantly alter the derived value of n. To prefer values above the mean for one gas and below it for the other, it is

necessary to show why the data selected are more reliable than the average (or minimum) values of the whole set of experimental diffusivities.

The data presented in Table 2 provide little evidence of n being close to unity and therefore for the appropriateness of the film model. This is not to say that the film model does not have its uses both conceptually and in pin-pointing the resistance of which phase is rate controlling for interfacial exchange and for calculating chemical enhancement of transfer in the aqueous phase. However, as expected, the model lacks physical reality except, possibly, under very calm conditions. On the other hand, a large majority of the exponents in the table fall in the range 0.5–0.8 (mean ~0.7), which covers the predictions of both the surface renewal and boundary-layer models. It is not possible to say which of these models is more favoured by the presently available data. Better discrimination between the models will have to await both improved experimental results and, especially, accurate redetermination of gas diffusivities.

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