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Measurement of the diffusion coefficient of sulfur hexafluoride in water

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Abstract. Sulfur hexafluoride has been widely used in field studies and laboratory experiments to develop a relationship between gas transfer and wind speed. The interpretation of the data from such studies requires the diffusion coefficient of SF₆ (D_{SF_6}), which has not previously been measured. In this study, D_{SF_6} has been determined in pure water and in 35‰ NaCl over a temperature range of 5-25°C. The measurements were made using a continuous-flow diffusion cell where SF₆ flows beneath an agar gel membrane while helium flows above the gel. The experimental data for pure water yielded the following equation: $D_{SF_6} = 0.029 \exp(-19.3/RT)$, where R is the gas constant and T is temperature in kelvins. Measurements of D_{SF_6} in 35‰ NaCl were not significantly different from the pure water values. On the basis of our data, we estimate the Schmidt numbers for seawater over the temperature range 5-25°C to be $Sc = 3016.1 - 172.00t + 4.4996t^2 - 0.047965t^3$, where t is temperature in degrees Celsius.

Introduction

Sulfur hexafluoride (SF₆) has been used extensively as a deliberate tracer in field and laboratory studies of air-sea exchange processes [Wanninkhof *et al.*, 1987; Upstill-Goddard *et al.*, 1990; Watson *et al.*, 1991; Asher *et al.*, 1992; Wanninkhof *et al.*, 1993]. SF₆ is an ideal tracer owing to its lack of chemical and biological reactivity, low natural levels, and low detection limit using gas chromatography with electron capture detection. The results of SF₆ studies have been used as the basis for deriving and testing a general relationship between wind speed and the gas exchange coefficient k , where

$$\text{Flux} = k(C_l - C_g / \alpha) \quad (1)$$

and C is the concentration in the liquid (l) or gas phase (g) and α is the dimensionless solubility of the gas in seawater [Liss and Slater, 1974]. In these tracer studies, SF₆ is released into surface ocean or lake waters, and the evasion of the gas is monitored by the decrease in surface mixed layer concentration. For dual-tracer studies the concentration of ³He is also monitored, and the rate of decrease in ³He/SF₆ is determined. There are significant differences between various expressions proposed for the magnitude and wind speed dependence of gas exchange [Smethie *et al.*, 1985; Liss and Merlivat, 1986; Wanninkhof, 1992], and this subject is currently the focus of some controversy.

The gas exchange coefficient has been found to be a function (f) of the diffusivity (D) of the gas in water according to the following relationship:

$$k_l = f(Sc^{-n}) = f(D^n) \quad (2)$$

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where k_l is the liquid phase gas exchange coefficient, Sc is the Schmidt number (kinematic viscosity/diffusivity), and n may vary from 1/2-2/3 depending on the sea state [Liss and Merlivat, 1986; Jähne *et al.*, 1987b].

In previous SF₆ studies, Sc for SF₆ (Sc_{SF_6}) was estimated using a diffusivity calculated from empirical relationships developed by Wilke and Chang [1955] and Hayduk and Laudie [1974]. These relationships fit diffusivity data for nonelectrolytes in dilute solutions as a function of the molar volume of the diffusing gas and the viscosity of the solvent. Estimates for the diffusivity have been used because D_{SF_6} has not previously been measured. In this study we measured the diffusivity of SF₆ (D_{SF_6}) in pure water and compare the results to the estimations from the empirical formulas. We also measured D_{SF_6} in 35‰ NaCl and discuss the implications for estimating Sc_{SF_6} in seawater.

Experimental Method

The experimental method for this measurement was based on the method developed by Barrer [1941]. The experimental method consists of monitoring the diffusion of a gas through an aqueous gel membrane (F-1). At steady state the flux of the gas through a planar membrane is given by the following expression:

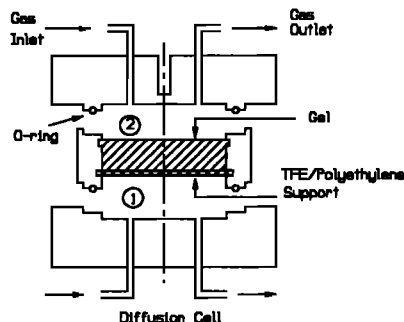
$$\Phi = \frac{D \cdot \Delta C}{l} \quad (3)$$

where ΔC is the concentration difference across the membrane, and l is the thickness of the gel (in centimeters). The flux can also be expressed in terms of the gas phase concentrations on either side of the gel if the solubility of the gas in water is known. The equation for the diffusivity of the gas can then be expressed as

$$D = \frac{C_{2g} f_2 l}{C_{1g} \alpha A} \quad (4)$$

where C_{2g} and C_{1g} are the gas phase concentrations above and

A.



B.

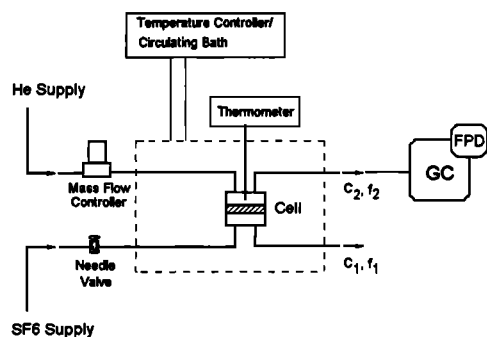


Figure 1. a) Schematic cross section of the diffusion cell. The high- and low-concentration chambers are labeled as 1 and 2, respectively, as in equation (4). b) Schematic of the experimental apparatus. The gas flows from the cell are labeled as in equation (4).

below the gel, respectively, f_2 is the flow through the upper chamber (in cubic centimeters per second), α is the Ostwald solubility of SF₆ in water (ratio of aqueous phase to vapor phase concentration), and A is the cross-sectional area of the membrane (in square centimeters).

The diffusion cell consists of a stainless steel housing with a chamber above and below an aqueous gel membrane (F-1a). This apparatus was developed from a design by Jähne *et al.* [1987a] for the determination of the diffusion coefficient of dimethylsulfide [Saltzman *et al.*, 1993]. The configuration was then modified for the measurement of D_{SF_6} . The membrane is prepared with 0.7% agar dissolved in pure water and is 3.8 cm in diameter and approximately 0.30 cm thick. For the NaCl gels, 0.75% agar was dissolved in a 35% aqueous NaCl solution. The gel is supported by a sheet of porous polytetrafluoroethylene filter membrane 0.13 mm thick with mean pore size 10–20 μm (Zitex, Norton Company, Wayne, New Jersey) and a sheet of porous polyethylene 1.59 mm thick with mean pore size 15–45 μm (X-4900, Porex Corporation, Fairburn, Georgia). Both sheets are sufficiently porous that they do not measurably inhibit diffusion.

The thickness of the gel used in each experiment was calculated using the weight of the gel and the diameter of the cell. The density of the pure water gel was found to be 0.992 g cm⁻³ ($1\sigma = 0.1\%$) at 25°C. For the NaCl gel the density was 1.019 g cm⁻³ ($1\sigma = 0.1\%$) at 25°C. Gel loss due to evaporation during the course of an experiment was approximately 1% by weight.

The thickness of the gel measured at the end of the experiment was used in the calculation of the diffusivity.

The cell was submerged in a stirred, thermostatted water bath, and experiments were run at 5, 15, and 25°C. While the cell was brought to the appropriate temperature, it was flushed with helium to remove air dissolved in the gel during preparation. At the onset of the experiment, pure SF₆ gas was introduced into the lower chamber at a flow rate of 5 cm³ min⁻¹, while the upper chamber was flushed with helium at the same flow rate. In order to maintain a constant gas flow rate through the upper chamber during the course of the experiment, a mass flow controller was used. The gas was allowed to diffuse through the gel until the concentration of SF₆ in the upper chamber reached a constant value, indicating that steady state had been reached. The outflow of the upper chamber was sampled every 1.5 min. Ten to twenty concentration measurements were averaged to obtain the steady state value.

The concentration in the upper chamber was determined relative to the concentration of SF₆ in the lower chamber. The outflow of the upper chamber was loaded into a Teflon loop (100- μ L STP) on a 10-port gas injection valve and determined using gas chromatography with flame photometric detection (FPD). The concentration of SF₆ in the upper chamber was calculated using calibration curves prepared through serial dilutions of the effluent of the lower chamber (pure SF₆) with He in a glass, gastight syringe. The uncertainty in the dilution process was of the order of 6% (1σ). Calibration curves were run before and after every experiment in order to account for drift in the response of the FPD. The curve run immediately after the experiment was used to calculate the percentage of SF₆ in the upper chamber. The analyses were done using an HP5890 gas chromatograph with a 1/8-inch OD, 1.25-m long stainless steel column packed with Porasil B 100/150 mesh (Alltech, Deerfield, Illinois), an oven temperature of 30°C, and a flow rate of helium carrier gas of 40 cm³ min⁻¹.

Agarose gels have been used extensively in the past in diffusion studies [Schantz and Lauffer, 1962; Spalding, 1969; Langdon and Thomas, 1971]. Jähne *et al.* [1987a] showed that experimental determinations of diffusivity using a gel were more reproducible than results obtained using a wetted-frit diaphragm. This is probably due to the lesser degree of convection and turbulence in the gel as compared with the diaphragm. However, the presence of the gel requires a correction. The gel decreases the solubility of the gas in the membrane and inhibits the diffusion path by the creation of a structure in the membrane. Langdon and Thomas [1971] have estimated that both of these effects combine to reduce the rate of diffusion by a factor of about 2% for a 0.7% gel. After the diffusion coefficient has been calculated the value is increased by a factor of 1.90% for pure water and 2.03% for a NaCl gel to correct for the presence of the gel.

The Ostwald coefficient of SF₆ in pure water was calculated using the equation from Wilhelm *et al.* [1977], based on the experimental data of Ashton *et al.* [1968]. The reported uncertainty in this measurement is less than 1% (1σ). The Ostwald coefficient of SF₆ in 35% NaCl was calculated using the salting-out coefficient k_s for SF₆ in NaCl at 25°C [Morrison and Johnstone, 1955] to correct the pure water solubilities. The estimated uncertainty in the Ostwald coefficient for NaCl at 25°C is of the order of 5% (1σ). At lower temperatures this uncertainty could be larger since k_s is not known at these temperatures. An important contribution to the uncertainty in this parameter is the temperature of the cell. The thermocouple used in

Table 1. Typical Values and Estimated Uncertainties in the Calculation of the Diffusivity of SF₆ in pure water

Parameter	Range	Absolute Uncertainty	Relative Uncertainty %
Flow rate, f_2 (in cm ³ sec ⁻¹)	0.088	0.0005	0.6
Concentration ratio, C_2/C_1	(2.8-3.5)×10 ⁻⁵	(1.0-1.3)×10 ⁻⁶	3.6
Temperature, T (in degrees C)	5-25	0.4	n/a
Ostwald coefficient for pure water, α	0.006-0.012	0.00003	0.8-2.1
Gel thickness, l (in cm)	0.30-0.31	0.005	1.6-1.7
Gel area, A (in cm ²)	11.51	0.002	0.02
Total			4.1-4.5

this experiment is accurate to $\pm 0.4^\circ\text{C}$. The combined effect of the measurement and the temperature result in an uncertainty in the Ostwald coefficient of 0.8-2.1% (1σ) for pure water and greater than 5% for NaCl.

The estimated uncertainty in a given calculation of D_{SF_6} in pure water is 4.1-4.5% (1σ) but 6.4-7.2% (1σ) for D_{SF_6} in NaCl. The largest contributors to this uncertainty are the concentration ratio, the solubility, and the calculated gel thickness. The range and estimated uncertainties for the parameters used in the determination of the diffusivity are listed in T-1.

Results and Discussion

Diffusivity of SF₆ in Pure Water

The diffusivity of SF₆ in pure water was measured at 5, 15, and 25°C during this study (F-2). These diffusivities can be related to temperature through the following expression:

$$D = Ae^{-Ea/RT} \quad (5)$$

where Ea is the "activation energy" for diffusion in water (in kilojoules per mole), $R=8.314 \times 10^{-3}$ kJ mol⁻¹ K⁻¹, and T is temperature in kelvins [Eyring, 1936]. A least squares fit of this function to the data obtained in this study yields a preexponential factor A of 0.029 cm² s⁻¹ ($1\sigma = 33\%$) and an Ea of 19.3 kJ mol⁻¹ ($1\sigma = 5.0\%$). The mean estimated uncertainty in this fit is 3.6% (1σ).

The experimental results are in reasonable agreement with empirical estimates of D_{SF_6} . The two most commonly used expressions for the estimation of diffusivity were proposed by Wilke and Chang [1955] (herein after referred to as W-C) ($D_{\text{W-C}}$) and Hayduk and Laudie [1974] (herein after referred to as H-L) ($D_{\text{H-L}}$) and are given below

$$D_{\text{W-C}} = \frac{7.4 \times 10^{-8} (\phi M_B)^{0.5} T}{\eta_B V_A^{0.6}} \quad (6)$$

$$D_{\text{H-L}} = \frac{13.26 (10^{-5})}{\eta_B^{1.4} V_A^{0.589}} \quad (7)$$

where ϕ is a dimensionless "association factor" equal to 2.6 for water, M_B is the molecular weight of solvent B , T is temperature (in kelvins), η_B is the viscosity of solvent B (in centipoise), and V_A is the molar volume (the volume of a mole of the pure liquid at its boiling point in cubic centimeters per mole) of the solute A . These expressions were obtained through empirical fits to measured diffusivities for a variety of gases in a variety of sol-

vents as a function of the molar volume of the gas and the viscosity of the solvent.

The calculated estimates of D_{SF_6} using these equations are shown in F-2. The estimates labeled as W-C (updated) are calculated using the W-C relationship with an association factor ϕ for water of 2.26 instead of the original value of 2.6. This change was recommended by H-L based on the larger data set available to them. The value for the viscosity of pure water was taken from Korson *et al.* [1969]. The molar volume of SF₆ used in these calculations is 77.69 cm³ mol⁻¹ [Wanninkhof *et al.*, 1985, 1987; Wanninkhof, 1992].

The estimates made using the W-C expression are in the best agreement with the measured values of D_{SF_6} , with the difference ranging from 0.6% at 5°C to 4.8% at 25°C. The W-C expression also provides a better prediction of the temperature dependence of the diffusivity than the H-L relationship. This is most likely due to the inclusion of temperature as an explicit parameter in the W-C expression. The discrepancy between the measured values and the H-L estimates ranges from only 1.2% at 25°C to 19.0% at 5°C.

Diffusivity of SF₆ in Sodium Chloride Solution

Diffusivities of SF₆ were also measured in an aqueous 35% NaCl solution at 5, 15, and 25°C (F-3). The measurements of

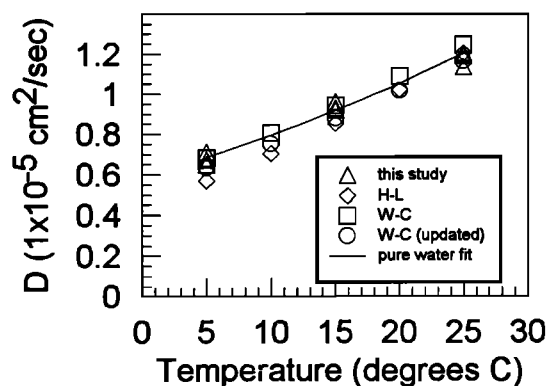


Figure 2. Diffusion coefficients of SF₆ in pure water as measured in this study and from estimates made from empirical expressions from Wilke and Chang [1955] and Hayduk and Laudie [1974]. Also plotted are the estimates from the Wilke-Chang relationship using an updated association factor for water proposed by Hayduk and Laudie [1974]. The curve is a fit to the experimental data taking the form $D=0.029 \exp(-19.3/RT)$, where R is the gas constant and T is temperature (in kelvins).

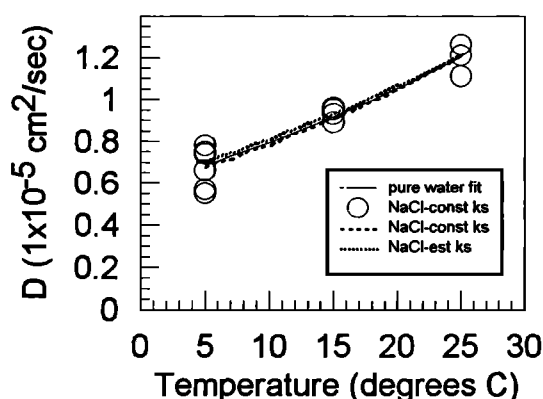


Figure 3: Diffusion coefficients of SF₆ in pure water and 35% NaCl as measured in this study. The solid line is a fit to the pure water data of the form $D=0.029 \exp(-19.3/RT)$, where R is the gas constant and T is the temperature (in kelvins). The dashed line is a fit to the NaCl data using a constant value for k_s (open circles) and takes the form $D=0.042 \exp(-20.2/RT)$. The dotted line is a fit to the NaCl data using k_s at 25°C and estimates for k_s at 5 and 15°C based on *Weiss* [1970] and takes the form $D=0.022 \exp(-18.7/RT)$.

D_{SF_6} in 35% NaCl gels exhibit considerably more scatter than those made in pure water gels. At 5°C the variance in the measurements ($1\sigma = 14\%$) is significantly greater than that predicted on the basis of experimental uncertainties (6-7%). The origin of this variance is not known. The solubilities used in the calculation of D_{SF_6} were obtained from the Setschenow relationship

$$\log S_0/S = k_s C \quad (8)$$

where S_0 and S are the solubilities of the gas in pure water and the salt solution, respectively, C is the concentration of the salt solution (in moles per liter), and k_s is the salting-out coefficient, which is specific to a salt-nonelectrolyte pair. The pure water solubilities were taken from *Ashton et al.* [1968], and the salting-out coefficient was measured by *Morrison and Johnstone* [1955]. The salting-out coefficient for SF₆ in NaCl has only been measured at 25°C ($k_s = 0.195$ L/mol), and this value was used to calculate D_{SF_6} at all temperatures. A least squares fit of the function given in (5) to D_{SF_6} calculated using a constant k_s results in a preexponential factor A of $0.042 \text{ cm}^2 \text{ s}^{-1}$ ($1\sigma = 66\%$) and an E_a equal to 20.2 kJ mol^{-1} ($1\sigma = 12.6\%$). The mean estimated uncertainty in this fit is 10.2% (1σ).

The salting-out coefficient, however, is not necessarily constant with respect to temperature. Gases such as nitrogen, oxygen, and argon exhibit an increase in k_s of the order of 15-16% with a decrease in temperature from 25 to 5°C [*Weiss*, 1970]. If we assumed that k_s for SF₆ varied in this manner, the calculated diffusivities at 5 and 15°C would increase by 4% and 2%, respectively, compared with the values obtained assuming constant k_s . A least squares fit to these diffusivities yields a preexponential factor A of $0.022 \text{ cm}^2 \text{ s}^{-1}$ ($1\sigma = 64\%$) and an E_a of 18.7 kJ mol^{-1} ($1\sigma = 13.1\%$) (F-3). The mean estimated uncertainty in this fit is 9.8% (1σ). It should be noted that gases like N₂, O₂, and Ar are not necessarily good models for predicting the behavior of larger, more polarizable molecules like SF₆ [*Masterton and Lee*, 1970].

At all temperatures the difference between D_{SF_6} in 35% NaCl and in pure water is not significant at the 95% confidence level, according to the t test [*Havlicek and Crain*, 1988]. This is surprising because diffusivity should be lower in NaCl than in pure water, owing to the increase in viscosity with increased ionic strength. This effect has been observed in previous studies of diffusivity. *Ratcliff and Holdcroft* [1963] measured the diffusivity of carbon dioxide (D_{CO_2}) in pure water and in various salt solutions at 25°C. They observed that diffusivity decreased with increasing salinity for all salts tested, including NaCl. Interpolating from their data, D_{CO_2} in a 35% NaCl solution was estimated to be about 6% lower than the pure water diffusivity. *Jähne et al.* [1987a] measured the diffusivities of H₂ and He in pure water and 35.5% NaCl from 5 to 35°C. They found diffusivities in the salt solutions to be lower by 5-8%, with the difference greatest at the lower temperatures. *Jähne et al.* [1987a] recommended an average correction of 6% when converting pure water diffusivities to seawater. *Saltzman et al.* [1993] compared the diffusivity of methane in 35% NaCl and in pure water at 15°C and found the values for NaCl to be 4% lower than the pure water diffusivities.

The calculated diffusivities of SF₆ in 35% NaCl at all temperatures imply that there is no difference in D_{SF_6} between pure water and NaCl solutions. The lack of a difference emphasizes the lack of understanding of the process of diffusion. There is no existing theory which can accurately predict the effect of parameters such as temperature and ionic strength on the diffusion of a gas through a liquid membrane.

Schmidt Number of SF₆ in Seawater

The results of this study suggest that the diffusivity of SF₆ in seawater should be similar to that in pure water. The Schmidt numbers (kinematic viscosity divided by diffusivity, ν/D) calculated for SF₆ in seawater using our pure water values over the temperature range 5-30°C are given in T-2. These Schmidt numbers were calculated using kinematic viscosities (ν , the ratio of molecular viscosity to density) calculated from the viscosity of seawater from *Millero* [1974] and the density of seawater from *Millero and Poisson* [1981]. The uncertainty in each Schmidt number is dominated by the uncertainty in the diffusivity and ranges from 4.1 to 4.5% (1σ) over the temperature range given in Table 2. A least squares third-order polynomial fit to the Schmidt number data yields the following equation:

$$Sc = 3016.1 - 172.00 t + 4.4996 t^2 - 0.047965 t^3 \quad (9)$$

where t is temperature (in degrees Celsius). The estimated uncertainty in this fit is 0.20% (1σ). *Wanninkhof* [1992] proposed a similar relationship for Sc_{SF_6} in seawater calculated from diffusivities estimated using the W-C relationship, with the updated association factor, and a reduction to those estimated diffusivities of 6%, based on the correction proposed by *Jähne et al.* [1987a]. Values for Sc_{SF_6} obtained using the *Wanninkhof* [1992] relationship are given in T-2. Our values for Sc are lower than those recommended by *Wanninkhof* [1992]. The difference is larger than the uncertainty in our values and ranges from 4.7% at 30°C to 12.4% at 5°C.

Summary

The diffusivity of SF₆ in pure water and 35% NaCl was measured in this study. The pure water results agree well with

Table 2. Schmidt Numbers for Sulfur Hexafluoride in Seawater of 35‰ Salinity

Temperature (degrees Celsius)	Schmidt Number (Sc, V/D) this study	Wanninkhof (1992)
5	2263	2544
10	1698	1849
15	1287	1379
20	992	1066
25	779	842
30	611	640

the empirical estimates. The expression from *Wilke and Chang* [1955], using the original association factor, provided the best agreement. The diffusivity measured in 35‰ NaCl is not significantly different from that in pure water, which is surprising in view of previous studies of other gases. It is possible, though not likely, that this effect is an artifact caused by assumptions about the salting-out coefficient of SF₆ in NaCl solution, which has not been experimentally determined at all temperatures. Better solubility data are needed to reduce some of the uncertainty in D_{SF_6} for NaCl. Recommended Schmidt numbers for SF₆ in seawater are given. The difference between experimentally determined D_{SF_6} and previous estimates used in air/sea exchange calculations are small, ranging from 1 to 20% over the temperature range 5-25°C. Since air/sea exchange is dependent on the square root of the diffusivity, these differences are minor.

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References

- Asher, W.E., P.J. Farley, R. Wanninkhof, E.C. Monahan, and T.S. Bates, Laboratory and field experiments on the correlation of fractional area whitecap coverage with air/sea gas transport, in *Precipitation Scavenging and Atmosphere-Surface Exchange*, vol. 2, *The Semonin Volume: Atmosphere-Surface Exchange Processes*, edited by S.E. Schwartz and W.G.N. Slinn pp. 815-828, Hemisphere, Washington, D.C., 1992.
- Ashton, J.T., R.A. Dawe, K.W. Miller, E.B. Smith, and B.J. Stickings, The solubility of certain gaseous fluorine compounds in water, *J. Chem. Soc. A*, 1793-1796, 1968.
- Barrer, R.M., *Diffusion in and through solids*, 464 pp., Cambridge University Press, London, 1941.
- Eyring, H., Viscosity, plasticity, and diffusion as examples of absolute reaction rates, *J. Chem. Phys.*, 4, 283-291, 1936.
- Havlicek, L.L., and R.D. Crain, *Practical Statistics for the Physical Sciences*, 489 pp., American Chemical Society, Washington, D.C., 1988.
- Hayduk, W., and H. Laudie, Prediction of diffusion coefficients for nonelectrolytes in dilute aqueous solutions, *AIChE J.*, 20, 611-615, 1974.
- Jähne, B., G. Heinz, and W. Dietrich, Measurement of the diffusion coefficients of sparingly soluble gases in water, *J. Geophys. Res.*, 92, 10,767-10,776, 1987a.
- Jähne, B., K.O. Münnich, R. Bosinger, A. Dutzi, W. Huber, and P. Libner, On the parameters influencing air-water gas exchange, *J. Geophys. Res.*, 92, 1937-1949, 1987b.
- Korson, L., W. Drost-Hansen, and F.J. Millero, Viscosity of water at various temperatures, *J. Phys. Chem.*, 73, 34-39, 1969.
- Langdon, A.C., and H.C. Thomas, Self-diffusion studies of gel hydration and the obstruction effect, *J. Phys. Chem.*, 75, 1821-1826, 1971.
- Liss, P.S., and L. Merlivat, Air-sea gas exchange rates: Introduction and synthesis, in *The Role of Air-Sea Exchange in Geochemical Cycling*, edited by P. Buat-Ménard, pp. 113-127, D. Reidel, New York, 1986.
- Liss, P.S., and P.G. Slater, Flux of gases across the air-sea interface, *Nature*, 247, 181-184, 1974.
- Masterton, W.L., and T.P. Lee, Salting coefficients from scaled particle theory, *J. Phys. Chem.*, 74, 1776-1782, 1970.
- Millero, F.J., Seawater as a multicomponent electrolyte solution, in: *The Sea*, vol. 5, *Marine Chemistry*, edited by E.D. Goldberg, pp. 3-80, John Wiley, New York, 1974.
- Millero, F.J. and A. Poisson, International one-atmosphere equation of state of seawater, *Deep Sea Res.*, 28A, 625-629, 1981.
- Morrison, T.J., and N.B. Johnstone, The salting out of nonelectrolytes, III, The inert gases and sulfur hexafluoride, *J. Chem. Soc.*, 3655-3659, 1955.
- Ratcliff, G.A. and J.G. Holdcroft, Diffusivities of gases in aqueous electrolyte solutions, *Trans. Inst. Chem. Eng.*, 41, 315-319, 1963.
- Saltzman, E.S., D.B. King, K. Holmen, and C. Leck, Experimental determination of the diffusion coefficient of dimethylsulfide in water, *J. Geophys. Res.*, 98, 16,481-16,486, 1993.
- Schantz, E.J., and M.A. Lauffer, Diffusion measurements in agar gel, *Biochemistry*, 1, 658-663, 1962.
- Smethie, W.M., Jr., T. Takahashi, D.W. Chipman, and J.R. Ledwell, Gas exchange and CO₂ flux in the tropical Atlantic Ocean determined from ²²²Rn and pCO₂ measurements, *J. Geophys. Res.*, 90, 7005-7022, 1985.
- Spalding, G.E., A sensitive method for measuring diffusion coefficients in agarose gels of electrolyte solutions, *J. Phys. Chem.*, 73, 3380-3383, 1969.
- Upstill-Goddard, R.C., A.J. Watson, P.S. Liss, and M.I. Liddicoat, Gas transfer velocities in lakes measured with SF₆, *Tellus, Ser. B.*, 42B, 364-377, 1990.
- Wanninkhof, R., Relationship between wind speed and gas exchange over the ocean, *J. Geophys. Res.*, 97, 7373-7382, 1992.

- Wanninkhof, R., J.R. Ledwell, and W.S. Broecker, Gas exchange-wind speed relation measured with sulfur hexafluoride on a lake, *Science*, 227, 1224-1226, 1985.
- Wanninkhof, R., J.R. Ledwell, W.S. Broecker, and M. Hamilton, Gas exchange on Mono Lake and Crowley Lake, California, *J. Geophys. Res.*, 92, 14,567-14,580, 1987.
- Wanninkhof, R., J.R. Ledwell, and A.J. Watson, Analysis of sulfur hexafluoride in seawater, *J. Geophys. Res.*, 96, 8733-8740, 1991.
- Wanninkhof, R., W. Asher, R. Weppernig, H. Chen, P. Schlosser, C. Langdon, and R. Sambrotto, Gas transfer experiment on Georges Bank using two volatile deliberate tracers, *J. Geophys. Res.*, 98, 20,237-20,248, 1993.
- Watson, A.J., R.C. Upstill-Goddard, and P.S. Liss, Air-sea gas exchange in rough and stormy seas measured by a dual-tracer technique, *Nature*, 349, 145-147, 1991.
- Weiss, R.F., The solubility of nitrogen, oxygen, and argon in water and seawater, *Deep-Sea Res.*, 17, 721-735, 1970.
- Wilhelm, E., R. Battino, and R.J. Wilcock, Low-pressure solubility of gases in liquid water, *Chem. Rev.*, 77, 219-262, 1977.
- Wilke, C.R. and P. Chang, Correlation of diffusion coefficients in dilute solutions, *A.I.Ch.E. J.*, 1, 264-270, 1955.
-
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