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 SF$_6$ ($D_{SF_6}$), 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 SF$_6$ 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 $Sc = 3016.1 - 172.00t + 4.4961t^2 - 0.0479657t^3$, where $t$ is temperature in degrees Celsius.

Introduction

Sulfur hexafluoride (SF$_6$) 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]. SF$_6$ 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 SF$_6$ studies have been used as the basis for deriving and testing a general relationship between wind speed and the gas exchange coefficient $k$, where

$$\text{Flux} = k \left( C_1 - C_2 / \alpha \right) \tag{1}$$

and $C$ is the concentration in the liquid ($l$) or gas phase ($g$) and $\alpha$ is the dimensionless solubility of the gas in seawater [Liss and Slater, 1974]. In these tracer studies, SF$_6$ 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 $^{3}$He is also monitored, and the rate of decrease in $^{3}$He/SF$_6$ 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:

$$k_l = f(Sc^{*}) = f(D^{*}) \tag{2}$$

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; Jahne et al., 1987b].

In previous SF$_6$ studies, $Sc$ for SF$_6$ ($Sc_{SF_6}$) 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 SF$_6$ ($D_{SF_6}$) 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 Barter [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:

$$\Phi = \frac{D \cdot \Delta C}{l} \tag{3}$$

where $\Delta C$ 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

$$D = \frac{C_{2g}f_l}{C_{1g}\alpha l} \tag{4}$$

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

![Diagram of Diffusion Cell](image)

**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).

B. 

below the gel, respectively, \( f_2 \) is the flow through the upper chamber (in cubic centimeters per second), \( \alpha \) is the Ostwald solubility of SF\(_6\) 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 Jahne 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 \( D_{\text{SF}6} \). The membrane is prepared with 0.7% agar dissolved in pure water and is 3.8 cm in diameter and approximately 0.30 \( \text{cm} \) 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 \( \text{mm} \) thick with mean pore size 10-20 \( \mu \text{m} \) (Zitek, Norton Company, Wayne, New Jersey) and a sheet of porous polyethylene 1.59 \( \text{mm} \) thick with mean pore size 15-45 \( \mu \text{m} \) (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 submersed 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 SF\(_6\) gas was introduced into the lower chamber at a flow rate of 5 cm\(^3\) 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 SF\(_6\) 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 SF\(_6\) in the lower chamber. The outflow of the upper chamber was loaded into a Teflon loop (100-\(\mu\) L STP) on a 10-port gas injection valve and determined using gas chromatography with flame photometric detection (FPD). The concentration of SF\(_6\) in the upper chamber was calculated using calibration curves prepared through serial dilutions of the effluent of the lower chamber (pure SF\(_6\) with He in a glass, gastight syringe). The uncertainty in the dilution process was of the order of 6% (1\(\sigma\)). 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 SF\(_6\) 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 cm\(^3\) min\(^{-1}\).

Agarose gels have been used extensively in the past in diffusion studies [Schantz and Laufer, 1962; Spalding, 1969; Langdon and Thomas, 1971]. Jahne 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 SF\(_6\) 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% (1\(\sigma\)). The Ostwald coefficient of SF\(_6\) in 35% NaCl was calculated using the salting-out coefficient \( k_s \) for SF\(_6\) 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 C is of the order of 5% (1\(\sigma\)). 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 cm³ 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, \( \alpha \) | 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 cm²)                     | 11.51          | 0.002                | 0.02                 |
| Total                                          | 4.1-4.5        |                      |                      |

this experiment is accurate to ±0.4°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 \( D_{SF₆} \) in pure water is 4.1-4.5% (1σ) but 6.4-7.2% (1σ) for \( D_{SF₆} \) 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 Table 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 (Figure 2). These diffusivities can be related to temperature through the following expression:

\[
D = A e^{-\frac{E_a}{RT}}
\]

where \( E_a \) is the "activation energy" for diffusion in water (in kilojoules per mole), \( R = 8.314\times10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1} \), 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 (1σ = 33%) and an \( E_a \) of 19.3 kJ mol⁻¹ (1σ = 5.0%). The mean estimated uncertainty in this fit is 3.6% (1σ).

The experimental results are in reasonable agreement with empirical estimates of \( D_{SF₆} \). The two most commonly used expressions for the estimation of diffusivity were proposed by Wilke and Chang [1955] (herein referred to as W-C) \( (D_{W-C}) \) and Hayduk and Laudie [1974] (herein referred to as H-L) \( (D_{H-L}) \) and are given below

\[
D_{W-C} = \frac{7.4\times10^{-9}(\phi M_B)^{0.1}T}{\eta_A V_A^{0.6}}
\]

\[
D_{H-L} = \frac{1326(10^{-4})}{\eta_A^2 V_A^{0.38}}
\]

where \( \phi \) 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), \( \eta_A \) 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 solvents as a function of the molar volume of the gas and the viscosity of the solvent.

The calculated estimates of \( D_{SF₆} \) using these equations are shown in Figure 2. The estimates labeled as W-C (updated) are calculated using the W-C relationship with an association factor \( \phi \) for water of 2.6 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 \( D_{SF₆} \), 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 (Figure 3). The measurements of
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 \cite{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. \textit{Rateiff 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. \textit{Jahne et al.} [1987a] measured the diffusivities of \( H_2 \) 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. \textit{Jahne et al.} [1987a] recommended an average correction of 5\% when converting pure water diffusivities to seawater. \textit{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 \( SF_6 \) 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 \( SF_6 \) in Seawater**

The results of this study suggest that the diffusivity of \( SF_6 \) in seawater should be similar to that in pure water. The Schmidt numbers (kinematic viscosity divided by diffusivity, \( \nu/D \)) calculated for \( SF_6 \) in seawater using our pure water values over the temperature range 5-30\°C are given in Table 2. These Schmidt numbers were calculated using kinematic viscosities (\( \nu \), the ratio of molecular viscosity to density) calculated from the viscosity of seawater from \textit{Millero} [1974] and the density of seawater from \textit{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\% (1\sigma) over the temperature range given in Table 2. A least squares third-order polynomial fit to the Schmidt number data yields the following equation:

\[
Sc = 3016.1 - 172.00t + 4.4996t^2 - 0.047965t^3
\]

where \( t \) is temperature (in degrees Celsius). The estimated uncertainty in this fit is 0.20\% (1\sigma). \textit{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 \textit{Jahne et al.} [1987a]. Values for \( Sc_{SF_6} \) obtained using the \textit{Wanninkhof} [1992] relationship are given in Table 2. Our values for \( Sc \) are lower than those recommended by \textit{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 \( SF_6 \) 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) | Wanninkhof (1992) |
|------------------------------|--------------------------|-------------------|
| 5                            | 2263                     | 2544              |
| 10                           | 1698                     | 1849              |
| 15                           | 1287                     | 1379              |
| 20                           | 992                      | 1066              |
| 25                           | 779                      | 842               |
| 30                           | 611                      | 640               |

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