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Measurements of the diffusion coefficients of CFC-11 and CFC-12 in pure water and seawater

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Abstract. Trichlorofluoromethane (CCl_3F ; CFC-11) and dichlorodifluoromethane (CCl_2F_2 ; CFC-12) have been widely used as tracers of oceanic circulation and mixing on decadal timescales. In order to estimate their transfer rate across the air-sea interface, liquid-phase diffusion coefficients are needed. In this study the diffusivities of CFC-11 and CFC-12 in pure water were measured over the temperature range 0.6–30°C. Diffusivities of CFC-11 in pure water ranged from $(5.24 \pm 0.25) \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ at 0.6°C to $(1.13 \pm 0.05) \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ at 30.3°C and a fit to the data yielded the equation $D_{\text{CFC-11}} = 0.015 \exp(-18.1/RT)$, where R is the universal gas constant in $\text{kJ mol}^{-1} \text{ K}^{-1}$ and T is the temperature in Kelvin. Diffusivities of CFC-12 in pure water ranged from $(5.38 \pm 0.22) \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ at 0.6°C to $(1.26 \pm 0.05) \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ at 30.3°C and the temperature dependence can be expressed as $D_{\text{CFC-12}} = 0.036 \exp(-20.1/RT)$. The estimated uncertainty in both equations is <3%. Experiments were also carried out in seawater for each compound. For CFC-11 the diffusivity in seawater was not significantly different from that in pure water. However, the diffusivity of CFC-12 in seawater was found to be $7.2 \pm 3.0\%$ lower than that in pure water. Schmidt numbers for both CFC-11 and CFC-12 in pure water and seawater were estimated from the data.

1. Introduction

Industrially produced CFC-11 (CCl_3F) and CFC-12 (CCl_2F_2) have well-known time histories of emissions and inferred atmospheric concentrations. In seawater they are chemically inert and have been shown to be useful tracers in the study of oceanic circulation and mixing on decadal timescales [Ganmon *et al.*, 1982; Bullister and Weiss, 1983; Weiss *et al.*, 1985; Fine *et al.*, 1988; Fine, 1993; Molinari *et al.*, 1992; Rhein, 1991, 1994]. They have also recently been found to be useful as tracers and age-dating tools for groundwater [Busenberg and Plummer, 1992; Busenberg *et al.*, 1993].

In most regions of the oceans, CFC-11 and CFC-12 concentrations in surface seawater are close to being in equilibrium with atmospheric concentrations [Bullister, 1984; Weiss *et al.*, 1985; Pickart *et al.*, 1989]. However, this is not always the case. Measurements in newly formed Labrador Sea water [Wallace and Lazier, 1988], the Greenland Sea [Rhein, 1991], the Weddell Sea [Bullister, 1989, the Ross Sea [Trumbore *et al.*, 1991], and the eastern Mediterranean Sea [Schlitzer *et al.*, 1991] have shown that equilibrium saturation is not achieved in high-latitude deep water formation areas and upwelling regions. In these cases, the oceanic uptake of CFC-11 and CFC-12 is controlled by their air-sea exchange rate. Air-sea gas transfer rates are determined by the air-sea concentration gradient and the transfer velocity, which reflects the physical state of the interface and the physical/chemical properties of the gas. Gas transfer velocities are commonly parameterized in terms of the Schmidt number of the gas [Holmen and Liss, 1984; Jahne *et al.*, 1987b]. The Schmidt number (Sc) is the ratio of the kinematic viscosity of seawater to the molecular diffusivity of

the gas in the liquid phase. Molecular diffusivities for CFC-11 and CFC-12 in water and seawater have not been determined experimentally. In this study the diffusivities of CFC-11 and CFC-12 in pure water and seawater were measured over the temperature range of 0.6°–30°C. The results were compared to predictions from semiempirical formulae.

2. Experimental Method

The experimental approach is based on the agar gel technique developed by Barrer [1941] and modified by Jahne *et al.* [1987a] and Saltzman *et al.* [1993]. The diffusion cell used in this experiment is a stainless steel housing, consisting of two chambers on either side of an aqueous gel membrane. Details of cell construction and operation were given by Saltzman *et al.* [1993]. In this experiment, CFC-11 or CFC-12 is passed continuously over one side of an aqueous gel membrane while helium flows across the other side. The concentration of CFC-11 or CFC-12 increases on the helium (low-concentration) side of the gel as the gas diffuses across the gel membrane.

At steady state the gas flux (Φ) through the gel is given by [Crank, 1975; Saltzman *et al.*, 1993]

$$\Phi = \frac{DC_1}{L} \quad (1)$$

where D is the diffusivity, L is the gel thickness, and C_1 is the aqueous gel concentration on the high-concentration side of the membrane. In terms of measurable parameters, the diffusivity can be expressed as [Saltzman *et al.*, 1993]

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

where C_{1g} and C_{2g} are the gas-phase concentrations on the high-concentration side and low-concentration side of the gel, respectively, f_2 is the gas flow through the low-concentration

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chamber, A is the gel cross-sectional area, and α is the dimensionless Ostwald solubility coefficient.

Gels were prepared by dissolving 0.7% agar in water or seawater, yielding measured densities of 0.992 g cm^{-3} ($1\sigma=0.1\%$) and 1.019 g cm^{-3} ($1\sigma=0.1\%$), respectively. The thickness of the gel membrane was calculated from the mass of the gel and the diameter of the cell (3.8 cm). Gel loss due to evaporation during an experiment was less than 1% by mass. The gel thickness at the end of the experiment was used in the calculation of the diffusion coefficient. Pure water experiments were carried out using Milli-Q water. Seawater experiments were carried out using Gulf Stream surface water, after filtration with $0.2 \mu\text{m}$ pore size membrane filters. The measured salinity of the seawater was 35.0‰ ($1\sigma=0.5\%$). Measured diffusion coefficients were increased by a factor of 1.9% for pure water and 2.0% for seawater to correct for the decreased solubility of CFC-11 and CFC-12 in the agar gel and hindrance of the three-dimensional agar structure [Langdon and Thomas, 1971].

The solubilities of CFC-11 and CFC-12 in water and seawater were obtained from Warner and Weiss [1985], with a quoted estimated accuracy and relative precision of 1.5% and 0.7% (1σ), respectively. In this experiment there was an additional uncertainty of 0.65% in the solubilities used for seawater due to the variation of salinity during the preparation of seawater gels.

The concentration of the diffusing gas was determined in the outflow of the low-concentration side of the cell by gas chromatography with photoionization (CFC-11) or thermal conductivity (CFC-12) detection. A 1/8" stainless steel Porasil B (100/150 mesh) column was used isothermally at 85°C with a carrier gas (helium) flow rate of 20 mL min^{-1} .

During an experiment the pressure in the diffusion cell is approximately 1 atm. The vapor pressure of CFC-11 is less than 1 atm at temperatures below about 24°C . To prevent CFC-11 condensing out in the cell on the high concentration side of the gel during an experiment, a 10% mixture of CFC-11 in ultrapure helium was used in all CFC-11 experiments. Since the vapor pressure of CFC-12 is significantly higher than 1 atm at all experimental temperatures, pure CFC-12 was used in all CFC-12 experiments.

Before each experiment, helium gas was introduced across both sides of the gel to remove the air dissolved in the gel during preparation. During the experiment the flow across the high-concentration side of the gel was kept at approximately 2 mL min^{-1} for CFC-11 and 5 mL min^{-1} for CFC-12. On the low-concentration side of the gel, the helium was mass flow controlled at a constant flow rate between 10 and 20 mL min^{-1} . Tests showed that the measured diffusivity was independent of flow rate in this range. The helium was bubbled through a water reservoir prior to the cell to saturate the helium stream with water vapor before entering the cell. This minimized evaporation of the gel during an experiment.

A stirred, thermostated water bath controlled the experimental temperature, between 0.6°C and 30°C . A mercury thermometer monitored the cell temperature in the bath with an estimated uncertainty of $\pm 0.1^\circ\text{C}$. When the experimental temperature was higher than room temperature, a counterflow Nafion membrane dryer (Permapure product) was used to dry the outflow of the low-concentration chamber. Measured concentrations were corrected for H_2O vapor loss in the dryer (3% at 25°C ; 4% at 30°C). Experiments were carried out with and without the dryer at room temperature to determine if CFC-11 or CFC-12 was lost in the dryer. No loss was observed.

A calibration was run immediately after each experiment by serially diluting the effluent of the high-concentration side of the gel with pure helium in glass gas-tight syringes. A tank of reference gas mixture (CFC-11 and He) was used to monitor day-to-day variation in detector response and to correct for changes in laboratory temperature and pressure.

Gas volumes and partial pressure-fugacity corrections were made to account for the nonideality of the pure CFC-12 used in these experiments. Two corrections were made to the data. First, the volume of pure gas used in the first stage of serial dilutions to generate calibration mixtures had to be corrected to account for CFC-12 molecule-molecule interactions. This correction increased the diffusivity by 1.9%. Second, a partial pressure-fugacity correction had to be made to the gas phase on the high-concentration side of the gel in order to use the solubility data of Warner and Weiss [1985]. Their measurements were made using a dilute gas phase. This correction also increased the diffusivity, ranging from 1.7% at 30.3°C to 2.4% at 0.6°C . Both these corrections are based on the virial equation of state expanded up to the second virial coefficient [Guggenheim, 1967] and follow the approach of Weiss and Price [1980]. Virial coefficients were obtained from Dymond and Smith [1980]. For CFC-11, deviations from ideality were negligible because the experiments were carried out in dilute mixtures of helium and were therefore essentially ideal.

The total uncertainty for a measured $D_{\text{CFC-11}}$ in pure water was estimated to be 3.7%-5.3% (1σ), with the largest contribution from the determination of the concentration ratio (C_{2g}/C_{1g}), which ranged up to 3.7%. The total uncertainty for a single measured $D_{\text{CFC-12}}$ was estimated to be 3.5% - 4.6% (1σ).

3. Results and Discussion

3.1. Diffusivity of CFC-11 and CFC-12 in Pure Water

The experimentally determined diffusion coefficients of CFC-11 and CFC-12 in pure water at 0.6° , 5° , 10° , 15° , 20° , 25° and 30°C are shown in Figure 1. Three replicates were carried out at each temperature. A least squares exponential fit to the data yields the equations:

$$D_{\text{CFC-11}} = 0.015 \exp(-18.1/RT) \quad \text{cm}^2 \text{ s}^{-1} \quad (3)$$

$$D_{\text{CFC-12}} = 0.036 \exp(-20.1/RT) \quad \text{cm}^2 \text{ s}^{-1} \quad (4)$$

Here R is the universal gas constant in $\text{kJ mol}^{-1} \text{ K}^{-1}$ and T is the temperature in Kelvin. The relative mean residuals for these fits are 1.3% (1σ) for $D_{\text{CFC-11}}$ and 1.4% (1σ) for $D_{\text{CFC-12}}$. Both equations have an estimated uncertainty of $<3\%$ (1σ).

Figure 1 also shows a comparison of our data with semiempirical estimates of the diffusivities of these compounds in pure water. The most commonly used expressions for estimating diffusivities of gases in aqueous solution are the formulae proposed by Wilke and Chang [1955] (D_{w-c}) and Hayduk and Laudie [1974] (D_{H-L}):

$$D_{w-c} = \frac{7.4 \times 10^{-8} (\phi M_B)^{0.5} T}{\eta_B V_A^{0.6}} \quad \text{cm}^2 \text{ s}^{-1} \quad (5)$$

$$D_{H-L} = \frac{13.26 \times 10^{-5}}{\eta_B^{1.4} V_A^{0.589}} \quad \text{cm}^2 \text{ s}^{-1} \quad (6)$$

Here ϕ is a dimensionless association factor equal to 2.6 for water, M_B is the molecular weight of water, T is the temperature in Kelvin, η_B is the viscosity of water in centipoise and V_A is the molar volume of the gas at its boiling point. The experimental

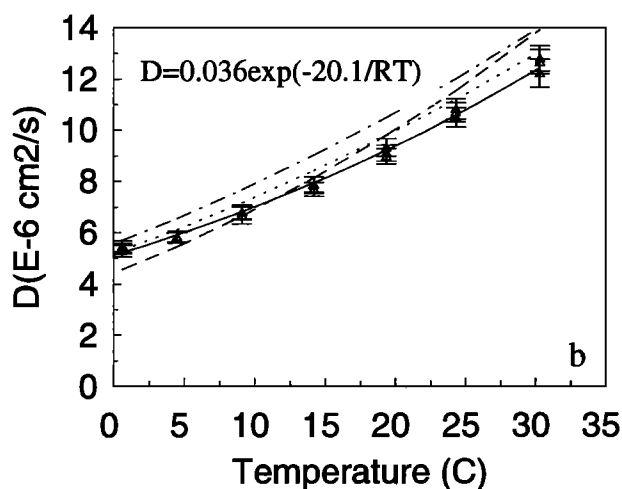


Figure 1. Diffusion coefficients of (a) CFC-11 and (b) CFC-12 in pure water as a function of temperature. Also shown are the fits to the data (solid line, this study) and the estimates from the empirical expressions proposed by *Wilke and Chang* [1955] (dot-dash line) and *Hayduk and Laudie* [1974] (dashed line). The updated Wilke Chang estimate (dotted line) is the Wilke-Chang estimate using an updated association factor for water recommended by *Hayduk and Laudie* [1974]. Read E-6 as 10^{-6} .

molar volume of CFC-12 is $80.7 \text{ cm}^3 \text{ mol}^{-1}$ [*Reid et al.*, 1987]. A value of $92.02 \text{ cm}^3 \text{ mol}^{-1}$ is used for CFC-11 in the calculation. This value is derived using the Tyn and Calus method [*Reid et al.*, 1987], which is generally accurate within 3%. A third estimate (updated Wilke-Chang (W-C)) is derived from the W-C equation, using an updated association factor of 2.26 for water recommended by *Hayduk and Laudie* [1974]. All three empirical estimates have average absolute errors of 5-10% [*Wilke and Chang*, 1955; *Hayduk and Laudie*, 1974].

The W-C expression is 2-14% and 6.2-11.6% higher than our measurements for CFC-11 and CFC-12, respectively. For CFC-11, the Hayduk-Laudie (H-L) estimate is 19.5% lower than our measurements at 0.6°C and 13.5% higher than our measurements at 30°C . For CFC-12, the H-L expression generates diffusion coefficients that are 14.8% lower than our measurements at 0.6°C and 10.8% higher than our measurements at 30°C . The updated W-C expression gives the best overall agreement with our data for both gases. For CFC-11 the expression is 6.6% lower than our measurement at 0.6°C and 6.3% higher at 30°C . For CFC-12 the updated W-C

expression is 1% lower than our measurement at 0.6°C and 4% higher at 30°C .

As mentioned in the introduction, air-sea gas transfer rates are commonly parameterized in terms of Schmidt numbers, where the Schmidt number is the kinematic viscosity of seawater divided by the diffusivity of the species. Using diffusivities generated from (3) and (4) and kinematic viscosities calculated from the pure water viscosities and densities of *Millero* [1974] and *Weast et al.* [1984], Schmidt numbers were calculated for CFC-11 and CFC-12 in pure water (Table 1). The uncertainty in each Schmidt number is dominated by the uncertainty in the diffusivity and is therefore estimated to be ~3%. A least squares polynomial fit to the calculated Schmidt numbers give the following expressions:

$$Sc_{\text{CFC-11}} (\text{pure water}) = 3423.5 - 208.63 t + 6.1544 t^2 - 0.07438 t^3 \quad (7)$$

$$Sc_{\text{CFC-12}} (\text{pure water}) = 3488.8 - 210.84 t + 5.7376 t^2 - 0.062371 t^3 \quad (8)$$

where t is the temperature in Celsius ($0.6^\circ - 30^\circ\text{C}$). Both fits have the same relative mean residual of 0.3% (1σ), and both equations have an estimated uncertainty of less than 3%.

3.2. Diffusivity of CFC-11 and CFC-12 in Seawater

The diffusivity of gases in liquids is strongly dependent on the viscosity of the liquid [*Wilke and Chang*, 1955; *Hayduk and Laudie*, 1974]. Over the temperature range from 5° to 30°C , the viscosity of seawater is 3-5% greater than that of pure water [*Millero*, 1974]. As shown in (5) and (6), seawater gas diffusivities are therefore expected to be smaller than the corresponding pure water diffusivities. There have been limited experimental studies of this effect. The expected reduction of diffusivity in seawater relative to pure water has been observed for He and H_2 by *Jahne et al.* [1987a], for CO_2 by *Ratcliff and Holdcroft* [1963], and for CH_4 by *Saltzman et al.* [1993]. Essentially no difference was observed between seawater and pure water diffusivities for SF_6 [*King et al.*, 1995] and for CH_3Br [*De Bruyn and Saltzman*, 1997]. These results are discussed in more detail by *King et al.* [1995].

Several runs were carried out using seawater gels to examine this effect for CFC-11 and CFC-12 (Table 2). Three runs at 9.4°C for CFC-11 gave a mean diffusion coefficient of $(6.80 \pm 0.12) \times 10^{-6} \text{ cm}^2 \text{ s}^{-1} (1\sigma)$. The corresponding pure water value is $(6.86 \pm 0.39) \times 10^{-6} \text{ cm}^2 \text{ s}^{-1} (1\sigma)$, which is not significantly different at the 95% confidence level. The same experiment was repeated at a later time, using the thermal conductivity detector (TCD) in place of the photoionization detector, with similar results. Four seawater runs at 12.6°C gave a mean diffusivity of

Table 1. Schmidt numbers, Calculated as Described in the Text, for CFC-11 and CFC-12 in Pure Water and 35‰ Seawater

T °C	Pure Water		Seawater	
	Sc _{CFC-11}	Sc _{CFC-12}	Sc _{CFC-11}	Sc _{CFC-12}
0	3424	3489	3502	3845
5	2507	2571	2577	2848
10	1883	1887	1948	2103
15	1441	1411	1498	1581
20	1116	1069	1168	1206
25	880	825	922	932
30	701	644	737	730

Table 2. Comparison Between Diffusion Coefficients in Pure Water and Seawater for CFC-11 and CFC-12

	Pure Water	Seawater	Difference
CFC-11 (9.4°C) ^a	6.86±0.39	6.80±0.12	No significant difference ^b
CFC-11 (12.6°C) ^c	7.62±0.21	7.47±0.18	No significant difference ^b
CFC-12 (9.1°C) ^c	6.75±0.17	6.26±0.12	-7.2±3.0%

Units $10^{-6} \text{ cm}^2 \text{ s}^{-1}$.^a Photoionization detector.^b At 95% confidence level (*t* test).^c Thermal conductivity detector.

$(7.47 \pm 0.18) \times 10^{-6} \text{ cm}^2 \text{ s}^{-1} (1\sigma)$. Four pure water runs gave a mean value of $(7.62 \pm 0.21) \times 10^{-6} \text{ cm}^2 \text{ s}^{-1} (1\sigma)$. Once again, these values are not significantly different at the 95% confidence level.

For CFC-12, the expected viscosity effect was observed. Four seawater runs at 9.1°C gave a mean diffusivity of $(6.26 \pm 0.12) \times 10^{-6} \text{ cm}^2 \text{ s}^{-1} (1\sigma)$. Three pure water runs at the same temperature gave a mean value of $(6.75 \pm 0.17) \times 10^{-6} \text{ cm}^2 \text{ s}^{-1} (1\sigma)$. This is 7.2±3.0% higher than the seawater value. The difference in behavior between CFC-11 and CFC-12 with respect to their diffusivity in seawater is not understood.

Assuming that the measured difference in diffusivity can be extrapolated to all temperatures, we have corrected our measured pure water diffusivities to generate seawater diffusivities as a function of temperature and have used the corrected diffusivities to calculate seawater Schmidt numbers for both CFC-11 and CFC-12 as a function of temperature (Table 1). No correction was made to the CFC-11 diffusivities, but the CFC-12 diffusion coefficients in pure water were decreased by 7.2% to generate seawater diffusivities. Seawater viscosities and seawater densities were obtained from *Millero* [1974] and *Millero and Poisson* [1981] respectively. A least squares polynomial fit to the resultant Schmidt numbers gives

$$Sc_{\text{CFC-11 (seawater)}} = 3501.8 - 210.31 t + 6.1851 t^2 - 0.07513 t^3 \quad (9)$$

$$Sc_{\text{CFC-12 (seawater)}} = 3845.4 - 228.95 t + 6.1908 t^2 - 0.067430 t^3 \quad (10)$$

The estimated relative mean residual of both these fits is 0.3% (1σ). If the difference between seawater and purewater diffusivities is, as assumed, constant as a function of temperature, then we estimate the overall uncertainty in (9) and (10) to be less than 3%.

Schmidt numbers based on empirically derived diffusion coefficients have often been used to estimate the air-sea exchange rate of CFC-11 and CFC-12 [*Trumbore et al.*, 1991; *Doney and Bullister*, 1992; *England et al.*, 1994; *Haine and Richards*, 1995]. *Wanninkhof* [1992] estimated Schmidt numbers for CFC-11 and CFC-12 in seawater based on the updated Wilke and Chang expression for diffusivities. In that study the estimated pure water diffusivities were decreased by 6% to yield the seawater values as suggested by *Jahne et al.* [1987a]. Overall Schmidt numbers estimated in this study agree reasonably well with the Schmidt numbers estimated by *Wanninkhof* [1992]. For CFC-12, the *Wanninkhof* [1992] Schmidt numbers are lower than the Schmidt numbers determined in this study, ranging from 7.6% lower at 30°C to 3.4% lower at 0°C. For CFC-11 the *Wanninkhof* [1992] Schmidt numbers are within 2% of Schmidt numbers

determined in this work above 25°C. Below 25°C they are higher, ranging from 4.3% higher at 20°C to 15% higher at 0°C.

As mentioned, Schmidt numbers determined in this work are calculated assuming the measured difference between seawater and pure water diffusivity at a single temperature can be extrapolated to all temperatures. In light of our inability to explain the lack of a difference between seawater and pure water diffusivity for compounds like CFC-11, it is difficult to assess the validity of this assumption. It would certainly be useful to measure seawater diffusivities across the whole temperature range. However, in earlier work with this apparatus [*King and Saltzman*, 1995] it was clear that measurement precision in seawater gels decreased at both ends of our measurable temperature range. The reason for this decrease in sensitivity is unknown. In future work we hope to examine and improve measurement precision in seawater gels to allow for the measurement of seawater diffusivities across a much wider temperature range.

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