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Molecular diffusion of CF_3SF_5 in pure water and artificial seawater

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21 8 **Molecular diffusion of CF₃SF₅ in pure water and artificial seawater**
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4 **Abstract.** We have experimentally determined the diffusion coefficient for trifluoromethyl sulfur
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6 pentafluoride (CF_3SF_5) in pure water and artificial seawater over a temperature range of $-2.0\text{ }^\circ\text{C}$
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8 to $30.0\text{ }^\circ\text{C}$. A working gas standard containing known concentrations of CF_3SF_5 and sulfur
9
10 hexafluoride (SF_6) was prepared. The working standard was allowed to diffuse across a water
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12 barrier, stabilized with agar gel, and the diffused gas was swept into a gas chromatograph with an
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14 electron-capture detector to measure the resulting gas mixing ratio. The mixing ratios for both
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16 CF_3SF_5 and SF_6 were measured to determine the diffusivity for each species. The diffusion
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18 coefficient for SF_6 was determined during these experiments as a check against existing literature
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20 values and to validate our experimental setup. The experimental data were fit to the Arrhenius
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22 equation to yield the following equations $D_{\text{CF}_3\text{SF}_5} = 0.0015\exp(-12.9/RT)$ and $D_{\text{SF}_6} =$
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24 $0.037\exp(-19.8/RT)$, where R is the gas constant in units of kilojoules per mole per kelvin
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26 and T is the temperature in kelvin. At the mean temperature of the ocean, $18\text{ }^\circ\text{C}$, $D_{\text{CF}_3\text{SF}_5} =$
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28 $7.02 \times 10^{-6} \pm 9.9\%$ and $D_{\text{SF}_6} = 1.03 \times 10^{-5} \pm 13.8\%$ cm^2/s . The diffusion coefficients for
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30 SF_6 matched the literature data within 4.3% for all temperatures.
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1 **Introduction**

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3 Trifluoromethyl sulfur pentafluoride (CF_3SF_5) is an inert halocarbon in the class of gases
4 collectively referred to as ignoble gases for the non-reactive properties they share with the noble
5 gases, but also for their potentially deleterious environmental impacts. For example, the
6 chlorofluorocarbons, also ignoble gases, are responsible for stratospheric ozone depletion
7 (Solomon, 1999). CF_3SF_5 is similar in many respects to sulfur hexafluoride (SF_6), a gas used
8 extensively in industry to electrically insulate high voltage equipment. Both CF_3SF_5 and SF_6
9 absorb radiation strongly in the infrared spectrum, making them greenhouse gases: CF_3SF_5 and
10 SF_6 have 18,000 and 23,900 times the global warming potential (GWP) of CO_2 , respectively
11 (Sturges et al., 2000). CF_3SF_5 has no known industrial use and its anthropogenic source remains
12 unknown. Its existence was previously thought to be the result of electrolytic degradation of
13 SF_6 ; however Pepi et al. (2005) determined that this is not the case. Globally, both gases exist at
14 the part per trillion level in the atmosphere and their concentrations are increasing at a rate of
15 about 6% per year (Suen, 2008).

16 The electronegativity (or insulating property) of these two gases makes them detectable at
17 extremely low concentrations by using gas chromatography with electron capture detection.
18 This, in combination with the fact that they are inert and nearly non-existent in the natural
19 environment, makes them potentially useful tracers for physical processes. SF_6 has been used
20 extensively in tracer release experiments (TREs), providing a better understanding to many
21 aspects of oceanography and environmental fluid mechanics (e.g., Ho et al., 2002; Ledwell et al.,
22 2000). Recently, Law and Watson (2001), Tanhua et al. (2004), and Bullister et al. (2006) have
23 determined that SF_6 can be potentially used as a transient tracer in the ocean, given its rate of

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1 monotonic increase in the atmosphere (Geller et al., 1997; Maiss and Brenninkmeijer, 1998).

2 There is currently a high demand for a new transient tracer because the previously used
3 chlorofluorocarbons have lost their effectiveness as a result of their declining atmospheric
4 mixing ratios. It can become problematic if SF₆ is used in both TREs and as a transient tracer,
5 because purposefully introduced SF₆ violates the boundary conditions provided by its well
6 known atmospheric time history. Therefore, CF₃SF₅ has been adopted as a new tracer for TREs,
7 so that SF₆ can become a dedicated transient tracer (Ho et al., 2008). Because of its potential
8 value as a transient tracer, the scientific community has declared a moratorium on deep ocean
9 tracer releases of SF₆ to avoid further contaminating the anthropogenic signal in the ocean.

10 Ho et al. (2008) determined that CF₃SF₅ has the potential to replace SF₆ in deep ocean TREs.
11 CF₃SF₅ has several properties that make it a potential tracer. As stated above, it shares many of
12 the ideal tracer properties with SF₆, and current experimental methods can be readily adapted to
13 include measurement of both CF₃SF₅ and SF₆, which utilize the same techniques for injection,
14 sampling, and analysis. Recently, the use of CF₃SF₅ has become more common; for instance the
15 species was released in Drake Passage to determine ocean mixing at mid-depths (Watson et al.,
16 2013). When interpreting the results of TREs with CF₃SF₅, it is valuable to determine the
17 physical properties of the tracer, including its diffusivity in water. In dual-tracer gas exchange
18 experiments, for instance, two tracers with different diffusivities are released simultaneously, and
19 the change in concentration ratio between the two species over time can determine gas exchange
20 rates (Watson and Ledwell, 2000). In this experiment we determine the diffusivity of CF₃SF₅ in
21 pure water as well as artificial seawater over a temperature range of -2°C to 30°C.

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23 **Experimental Method**

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6 2 We have reproduced the experimental configuration used by King and Saltzman (1995),
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9 3 including use of the same diffusion cells, which were provided by Eric Saltzman. The
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11 4 experimental method was based on the ideas developed by Barrer (1941). A gas standard of
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14 5 known composition is allowed to diffuse across a water barrier while the concentration of the
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16 6 diffused gas is monitored on the other side of the cell. At steady state, the flux across the water
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19 7 barrier takes the form of Fick's First Law:

$$\Phi = \frac{D\Delta C}{l} \quad (1)$$

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24 9 where Φ is the flux, D is the diffusion coefficient, ΔC is the difference in concentration across
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27 10 the water barrier, and l is the height of the water barrier (King and Saltzman, 1995). Since the
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29 11 solubility of CF_3SF_5 in water has been determined by Busenberg and Plummer (2008), the flux
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32 12 can be rewritten in terms of the gas solubility on each side of the water barrier. The diffusion
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34 13 coefficient for CF_3SF_5 in water can then be expressed as:

$$D = \frac{X_2 f_2 l}{X_1 \alpha A} \quad (2)$$

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40 15 where X_1 is the gas mixing ratio before diffusing through the water barrier, X_2 is the gas mixing
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42 16 ratio after diffusing through the water barrier, f_2 is the volumetric flow rate of the diffused gas, α
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45 17 is the Ostwald solubility, and A is the cross-sectional area of the water barrier (Figure 1).

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47 18 The primary experimental challenge with measuring the aqueous diffusivity of gas arises from
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50 19 the large difference in gas concentration between X_2 and X_1 . For sparingly soluble gases, such
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52 20 as these, X_2 can be five orders of magnitude smaller than X_1 . A working gas standard
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55 21 containing CF_3SF_5 and SF_6 was prepared by serial dilutions using pressurized N_2 gas as the
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57 22 primary diluent. The targeted mixing ratios for CF_3SF_5 and SF_6 were 119 ppmv and 476 ppmv,
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59 23 respectively. These mixing ratios were chosen to produce a value for X_2 that would be in the
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1 calibration range of our third party gas standards. SF₆ was included in the working standard, as
2 its diffusion coefficient could be determined to validate the experiment; the diffusion coefficient
3 for SF₆ was determined and compared to the values obtained by King and Saltzman (1995).

4 To measure the exact concentration in our working gas standard (X_i) it was necessary to
5 serially dilute the standard before injecting it directly into the gas chromatograph. Two Kimax[®]
6 1000 ml flasks were weighed, filled with DI water at room temperature, and then reweighed to
7 accurately determine their volumes. The flasks were then purged with nitrogen at 5 psi for 5
8 minutes before being covered at atmospheric pressure with septum stoppers. A Hamilton
9 MICROLITER[™] syringe was used to inject the flasks with known volumes between 150-300 μl
10 of the standard gas, making the pressure within the flasks marginally above atmospheric. We
11 assumed that the septum stoppers absorbed or released very little amounts of gas. The potential
12 contamination of the standard by adsorption and release of gas was not particularly significant
13 because the concentration of the gas was approximately the same within the flask between trials.
14 We equipped a 50 mL syringe with a needle to penetrate the septum stoppers and obtain the gas.
15 The diluted gas solution was then injected into a VICI[®] 8-port valve where it loaded a 25 μl
16 sample loop. Ultra high purity nitrogen purged the gas in the sample loop into a SRI 8610C gas
17 chromatograph (GC) with an electron capture detector (ECD). The concentration of the diluted
18 gas was determined by linearly interpolating between data points on a calibration curve for
19 CF₃SF₅ (Figure 2) and another calibration curve for SF₆ (Figure 3). The calibration curves were
20 prepared by injecting a 7.7 ppbv CF₃SF₅ standard and a 155.9 ppbv SF₆ standard into 10 μl, 25
21 μl, 100 μl, 0.25 ml, and 1.0 ml, sample loops. Three trials were conducted for each sample loop
22 size, and the ECD consistently produced peak areas within a 0.5% relative error. To account for
23 the drift in the ECD readings over time, the peak areas for each concentration measurement were

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1 bracketed by two points on the calibration curves within a few days. The use of a local
2 piecewise linear fit rather than a polynomial fit was deemed satisfactory due to the proximity of
3 each calibration point on the curve; therefore complete calibration curves utilizing the entire
4 range of sample loop sizes were not prepared regularly. The dilution step of the standard gas was
5 designed to locate the peak areas of the diluted gas in regions of the calibration curves where
6 concentrations of each gas component could be accurately measured.

7 The gas mixing ratio at the outlet of the diffusion cell (X_2) was determined using the
8 experimental method illustrated in Figure 1. The standard gas flowed from its gas cylinder,
9 through 1/8 inch inner diameter stainless steel tubing and into a flow controller (Cole Parmer
10 32907-67) to meter the gas at 0.003 standard liters per minute. The flow of gas then passed
11 through 1/8 inch inner diameter vinyl tubing and into a diffusion cell housing the water barrier.
12 The diffusion cell consists of a lower chamber below the water barrier and an upper chamber
13 above the water barrier. The water barrier is supported by a porous hydrophobic filter membrane
14 and a thin sheet of porous polyethylene (King and Saltzman, 1995). The rate of diffusion
15 through the polyethylene sheet was assumed to be much greater than the rate of diffusion
16 through the water barrier, and therefore the effects of the polyethylene sheet were negligible. The
17 undiffused gas passed through the lower chamber and was vented to the atmosphere. The
18 standard gas diffused from the lower chamber, through the water barrier, and into the upper
19 chamber of the diffusion cell. A continuous flow of Ultra High Purity nitrogen then swept the
20 diffused gas from the upper chamber into a VICI 8-port valve equipped with a sample loop.
21 Before a sample was analyzed, a solenoid valve closed for 30 sec to let the total pressure in the
22 VICI valve equilibrate to atmospheric pressure. Finally, the VICI valve was rotated to introduce
23 the sample onto the GC column for analysis. The concentration of the diffused gas was

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1 determined by linearly interpolating data points on the calibration curves. The operating
2 conditions were designed to position the peak areas of CF_3SF_5 and SF_6 in the same region on the
3 calibration curves as the X_1 measurements. The peak areas in the diffusivity experiments were
4 bracketed by points on the calibration curves every few days to account for any drift in the ECD
5 readings. Two trials for CF_3SF_5 concentration measurements (one trial at $-2\text{ }^\circ\text{C}$ and another trial
6 at $15\text{ }^\circ\text{C}$) were slightly outside the range of calibration; however they were very close to a
7 measured peak area and therefore their concentration measurements were deemed accurate. The
8 accuracy of these trials was verified by the fact that the resulting diffusivity measurements
9 agreed with the measurements of other trials. The uncertainty in concentration measurements of
10 CF_3SF_5 and SF_6 were approximated to be 12.4% and 13.8%, respectively by applying the method
11 of least squares to the ranges that were used in the calibration curves. The error in the
12 concentration ratio (X_2/X_1) was reduced, however, since the measurements for X_2 and X_1 fell
13 within the same region of the curves. The concentration values were likely overestimated
14 considering that a polynomial fit would result in concentrations less than a piece-wise linear fit
15 of the same data set. This overestimation, however, was divided out to some extent when X_2 was
16 divided by X_1 . Therefore, the error in the concentration ratios was less than the error in the
17 concentration measurements, though the error in the concentration ratios cannot be quantified
18 analytically. The concentration of the diffused gas was measured every 14 minutes to monitor
19 when the diffusion process reached steady state. The process took 4-14 hours to reach steady
20 state depending on the temperature and thickness of the water barrier in the diffusion cell.

21 The water barrier consisted of an agar solution approximately 0.8% by mass. A gas permeable
22 Millipore 10 μm membrane filter was used to support the agar solution in the diffusion cell. The
23 height of the water barrier (l) was determined by measuring the mass of the agar solution placed

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1 into the diffusion cell. We varied the water barrier height between trials to prevent the standard
2 gas from penetrating through the space in between the water barrier and diffusion cell. The
3 variability in height was accounted for using the proportionality between water barrier thickness
4 and diffusivity. The mass of the agar solution after the diffusion process was used to calculate
5 the gel thickness. Thomas and Langdon (1971) determined that the use of agar solution rather
6 than pure water decreased the calculated diffusion coefficients by approximately 1.9%.
7 Therefore, all the diffusion coefficients were increased by 1.9% to account for the effect of the
8 agar solution. The flow rate of the diffused gas (f_2) was metered at the inlet to the top of the
9 diffusion chamber using a (Cole Parmer 32907-67) flow controller. Depending on the
10 temperature of each trial, we set the nitrogen flow rate between values of 0.004 and 0.020 liters
11 per minute. Higher flow rates generally corresponded to lower temperatures. The flow of gas
12 across the water barrier was held constant during an experiment. We adjusted the flow rate, f_2 ,
13 of nitrogen to control the moles of gas that collected in the sample loop. We chose appropriate
14 flow rates of nitrogen for each trial to position the measured ECD readings within the calibrated
15 range. The Ostwald solubilities for SF_6 and CF_3SF_5 were determined using relationships
16 developed by Bullister et al. (2002) and Busenberg and Plummer (2008). The solubility
17 determinations for SF_6 in pure water and seawater occurred over a temperature range of 0°C to
18 40°C . Here, we have applied the solubility relationships for SF_6 slightly outside the range of
19 determination, when measuring diffusivity at -2°C . The Ostwald solubility of CF_3SF_5 in pure
20 water (α) was measured over a temperature range of 1°C to 35°C , and again, we applied our
21 solubility relationship slightly outside the range of determination when measuring diffusivity at -
22 2°C . The Ostwald solubility of CF_3SF_5 in seawater, however, was not measured and therefore an
23 approximate value was determined. We found the solubility ratio of CF_3SF_5 to SF_6 in pure water

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1 and assumed that the same solubility ratio applied for seawater. The solubility ratio,
2 $CF_3SF_5:SF_6$, was 0.53,0.54, 0.53, and 0.48 at temperatures of -2°C, 3°C, 15°C, and 30°C,
3 respectively. Solubility decreased with temperature for all temperature ranges except for -2°C to
4 3°C; this indicates uncertainty in extrapolating measurements for solubility beyond the measured
5 data set. The adjustment of the nitrogen flow increased the pressure within the upper chamber
6 of the diffusion cell by at most 0.37 kPa above atmospheric pressure for some trials in this study.
7 The small increase in pressure was measured using the (Cole-Parmer 32907-67) flow controller
8 located on the tubing leading up to the upper chamber of the diffusion cell. The flow of the
9 standard gas increased the pressure within the lower chamber of the diffusion cell by at most
10 0.04 kPa above atmospheric pressure and was measured using the (Cole-Parmer 32907-67) flow
11 controller leading up to the lower chamber of the diffusion cell. We assumed that the total
12 pressures measured by the two flow controllers were equal to the total pressure in the upper and
13 lower chambers of the diffusion cell. We adjusted the resulting estimate of the Ostwald
14 solubility to account for this increase in pressure in the lower chamber of the cell. The surface
15 area of the water barrier (A) was determined by measuring the diameter of the diffusion cell.

16 Stable temperature was maintained using a constant temperature bath filled with saltwater to an
17 approximate salinity of 40 ppt, to allow the bath water to be cooled to -2.0 °C. The temperature
18 of the diffusion cell was closely monitored using an Omega 1PT100K3515 100 Ohm 4-wire
19 RTD taped to the outside of the cell. The high thermal mass of the stainless steel diffusion cell
20 added an additional measure of thermal stability. Diffusion experiments were conducted at -2.0
21 °C, 3.0°C, 15.0°C and 30.0°C in DI water, and again at the same temperatures using a 35 ppt
22 solution of Instant Ocean[®] artificial seawater to find the diffusion coefficient in seawater over the
23 same range in temperature. Salinity was measured with a YSI Pro Plus multiparameter meter

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1 with conductivity sensor. Two trials in DI water and two trials in artificial seawater were
2 completed at each temperature, for a total of N = 4 separate determinations of the diffusion
3 coefficient of CF_3SF_5 and SF_6 at each temperature, except at -2°C where two trials were
4 completed in DI water and one trial was completed in artificial seawater.

5 Considering the uncertainty in the concentration ratio (stated above) as well as the uncertainties
6 in the gel thickness and solubility, we estimate the uncertainty of a diffusivity experiment to be
7 at most 18-19 % for the diffusivity measurements of SF_6 and CF_3SF_5 . These uncertainties were
8 determined using the error in concentration of the gases rather than the error in concentration
9 ratio of the gases. Since the error in concentration ratio was less than the error in gas
10 concentration, as stated above, the uncertainties are likely overestimated. Although the
11 concentration measurement was more accurate for CF_3SF_5 than SF_6 , the solubility was less
12 accurate because the solubility in seawater was not directly measured. As a result, the estimated
13 uncertainties were approximately equal for each species.

15 **Results and Discussion**

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17 The concentrations of CF_3SF_5 and SF_6 in the working standard were found to be 1716 and 776
18 ppmv respectively. The reason that the CF_3SF_5 concentration greatly exceeded the target
19 concentration is not known, but may be the result of an incomplete step in the gas standard
20 preparation, which was carried out without direct analytical control of the gas mixing ratio. The
21 dilution step involved in determining the standard gas concentration introduced an uncertainty of
22 2.9% for CF_3SF_5 and 3.5% for SF_6 in the diffusivity values.

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4 1 The thickness of the water barrier varied from 0.33-0.57 cm with an average value of
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6 2 0.45±0.073 cm between trials. The surface area of the diffusion cell was determined to be 11.7
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14 5 **Diffusion in DI water and seawater**
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19 7 The measured diffusivity for each species in seawater was similar to the measured diffusivities
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21 8 in DI water (Figures 4 and 5). The observed differences between the seawater and DI water
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24 9 trials were not systematic, and it was not possible to separate the variability introduced from
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26 10 experimental error. This result for SF₆ agreed with the work of King and Saltzman (1995)
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29 11 where there was also no consistent difference in the SF₆ diffusion coefficient between pure and
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31 12 salt water. It is generally expected for diffusivity to be lower in seawater than in pure water due
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34 13 to seawater's increased ionic strength and viscosity. This demonstrates the lack of knowledge
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36 14 about the diffusion process. There is no current theory that can accurately predict the effect of
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39 15 ionic strength on the diffusion of a gas through a liquid barrier. Consequently, we report the
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41 16 diffusivity values and statistics after aggregating the saltwater and DI water trials.
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45 18 **Diffusion of SF₆ in water**
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51 20 The diffusion coefficient can be related to temperature with the Arrhenius equation, as shown
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53 21 below:

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$$D = A \exp\left(-\frac{E_a}{RT}\right) \quad (3)$$

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1 where E_a is the activation energy in kilojoules per mole, R is the gas constant in kilojoules per
2 mole per kelvin, T is the temperature in kelvin, and A is the preexponential factor in square
3 centimeters per second. The values for the activation energy and preexponential factor are
4 determined using the best linear fit to the natural log of diffusivity (dependent variable) and the
5 reciprocal of temperature (independent variable). The activation energy was found to be 19.8 kJ
6 mole⁻¹ and the preexponential factor was found to be 0.037 cm² s⁻¹ for the diffusivity of SF₆ in
7 water. The overall uncertainty of this fit was $1\sigma = 13.8\%$, as determined by applying the method
8 of least squares to the Arrhenius model. The measured data points and equation are shown
9 alongside the equation from King and Saltzman (1995) in Figure 4.

10 The measured SF₆ diffusion coefficients were slightly larger than the values measured by King
11 and Saltzman (1995). The diffusivity given from our equation was approximately 1.8%, 2.2%,
12 3.1%, and 4.3% larger than the diffusivity from these authors' equation at temperatures of -2.0
13 °C, 3.0 °C, 15.0 °C, and 30.0 °C, respectively. The discrepancy between our data and the data of
14 King and Saltzman (1995) is within our experimental uncertainty and therefore deemed to be an
15 acceptable agreement. King and Saltzman (1995) determined diffusivity of SF₆ over a
16 temperature range of 5.0 °C to 25.0 °C, which we extrapolated to a range of -2.0 °C to 30.0 °C.

17 In this experiment the standard error between trials of the same temperature at -2.0 °C, 3.0 °C,
18 15.0 °C, and 30.0 °C were 8.2%, 6.5%, 10.6%, and 3.5%, respectively. The uncertainty can be
19 attributed to several factors. Primarily, there was error in the determination of concentrations
20 from the calibration curves. Furthermore, the hydrophobic Millipore membrane filters repelled
21 the agar solution in the diffusion cell, creating a slightly variable agar gel thickness. In addition,
22 there was some error in integrating the peak areas produced by the ECD; for instance some water
23 in the agar gel evaporated at higher temperatures, which produced broad peaks that altered the

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4 1 baseline for peaks produced by SF₆. Lastly, there was error in the solubility values due to the
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6 2 pressure gradient across the diffusion cell as well as the extrapolation of solubility values to a
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8 3 temperature range that was not directly measured. The solubility of SF₆ decreased with
9
10 4 increasing temperature, and consequently, lower temperatures resulted in more transport of SF₆
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12 5 into the ECD than higher temperatures. We aimed to control the transport of gas into the ECD
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14 6 by adjusting the N₂ flow rate (f_2); however, some trials at lower temperature resulted in greater
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16 7 peak areas on the calibration curves than higher temperatures. The calibration of large peak
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18 8 areas was less accurate than the calibration of small peak areas because the calibration curves
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20 9 developed curvature as peak area increased. Consequently, measured diffusivities tended to have
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22 10 lower values for standard deviation at higher temperatures than lower temperatures.
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31 12 **Diffusion of CF₃SF₅ in water**

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36 14 The activation energy and preexponential factor were found using the same method as SF₆ and
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38 15 were found to be 12.9 kJ mole⁻¹ and 0.0015 cm² s⁻¹, respectively. The overall uncertainty was
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40 16 $1\sigma=9.9\%$. The results are presented graphically in Figure 5. The standard error between trials of
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42 17 the same temperature at -2.0 °C, 3.0 °C, 15.0 °C, and 30.0 °C were 8.5%, 7.2%, 5.4%, and 1.7%,
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44 18 respectively. The uncertainty can be attributed to the same variability in the analytical procedure
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46 19 as stated above.
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50 20 The value of D for CF₃SF₅ was approximately 25% less than the value of D for SF₆ in the
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52 21 temperature range of -2.0 °C to 15.0 °C, and approximately 35% less than the D for SF₆ at 30.0
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54 22 °C. Based on the Graham's Law relationship, which relates molecular kinetics to the square root
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56 23 of the reciprocal of molecular mass, it makes sense for CF₃SF₅ to have lower diffusivity than SF₆
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1 in water due to its larger molecular mass. We applied Graham's Law to our measured
2 diffusivities of SF₆ to determine theoretical diffusivities for CF₃SF₅. We then plotted the
3 measured diffusivities for CF₃SF₅ against the theoretical values from Graham's Law, as shown in
4 Figure 6. Diffusivity for CF₃SF₅ was generally less than expected from Graham's Law,
5 particularly at high temperatures. Graham's Law is known to approximately model the diffusion
6 process, and therefore, the deviation from Graham's Law is reasonable. At temperatures of -2.0
7 °C, 3.0 °C, 15.0 °C, and 30.0 °C, the measured CF₃SF₅ diffusivity was 5.0%, 7.0%, 18.6%, and
8 30.7% less than the theoretical Graham's Law value, respectively. Therefore, the deviation from
9 Graham's Law increases with temperature. Previous estimates for CF₃SF₅ diffusivity that were
10 obtained by applying Graham's Law to the SF₆ diffusivity model from King and Saltzman
11 (1995) are also overestimated; at the mean temperature of the ocean, 18 °C, the theoretical value
12 for CF₃SF₅ diffusivity is 22.9% greater than our determined value. Consequently, studies that
13 estimated CF₃SF₅ diffusivity from Graham's Law relationships would benefit from a
14 reevaluation of data using the diffusivity values measured in this experiment.

16 **Impacts of measured diffusivities**

18 Based upon our experimental setup and the estimated uncertainty in D_{SF6} (13.8%), we do not
19 conclude that the 5% increase in D_{SF6} is significantly different from the previous results of King
20 and Saltzman (1995). Here, we included SF₆ as a test of the reproducibility of the method and as
21 a confirmation that our experimental configuration was consistent with previous experiments.
22 Knowledge of the effective diffusivity of CF₃SF₅ is pertinent information for the potential
23 candidate's use as a gas-exchange tracer, similar to the way SF₆ is currently used. The

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1 information is also important to estimate tracer loss if CF_3SF_5 is to be used in mixing
2 experiments (e.g., Ho, 2002). Although the diffusivity of CF_3SF_5 is lower than expected, it still
3 may not be practical to consider CF_3SF_5 and SF_6 as a practical tracer duet for open ocean dual
4 tracer experiments. Currently ^3He and SF_6 are used for dual tracer experiments; however ^3He is
5 difficult to measure, so an alternative pairing is desirable. Nevertheless, the evolution of the
6 concentration ratio of SF_6 and CF_3SF_5 is less than 20% in 30 days, as compared with a change of
7 94% in the concentration ratio of ^3He and SF_6 (Figure 7).

8

9 **Conclusion**

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11 The diffusivity for SF_6 and CF_3SF_5 in pure water and artificial seawater was measured over a
12 temperature range of $-2\text{ }^\circ\text{C}$ to $30\text{ }^\circ\text{C}$. The diffusivity of each species did not differ considerably
13 between pure water and seawater; therefore the Arrhenius equation models were used to fit
14 diffusivity in pure water and seawater equally well. This result agreed with previous studies,
15 where the diffusion coefficient for SF_6 did not consistently differ between pure water and
16 seawater. The measured diffusivity of SF_6 in water followed the expression: $D_{\text{SF}_6} =$
17 $0.037\exp(-19.8/RT)$ with an overall uncertainty of 13.8% in the fit of the model to the data.
18 Similarly, the measured diffusivity of CF_3SF_5 in water followed the expression: $D_{\text{CF}_3\text{SF}_5} =$
19 $0.0015\exp(-12.9/RT)$ with an overall uncertainty of 9.9% in the fit of the model to the data.
20 The measured diffusion coefficient for SF_6 in water was in reasonable agreement with previous
21 studies, validating the method used to measure the diffusion coefficient for CF_3SF_5 . Previous
22 estimates for CF_3SF_5 diffusivity from Graham's Law relationships overestimate diffusivity, and
23 therefore a reevaluation of data using measured values for diffusivity would be beneficial.

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4 1 Although the measured diffusivity for CF_3SF_5 is lower than expected, it is not practical to use
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6 2 CF_3SF_5 and SF_6 together in dual tracer experiments because their values for diffusivity do not
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9 3 promote a rapid evolution in concentration ratio. The use of CF_3SF_5 in TREs will become more
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11 4 common as SF_6 becomes a dedicated transient tracer, and therefore, the measured diffusivity of
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14 5 CF_3SF_5 in water is significant; the measurements in this experiment provide researchers
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16 6 improved accuracy in the data analysis of TREs.
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37 38 15 **References**

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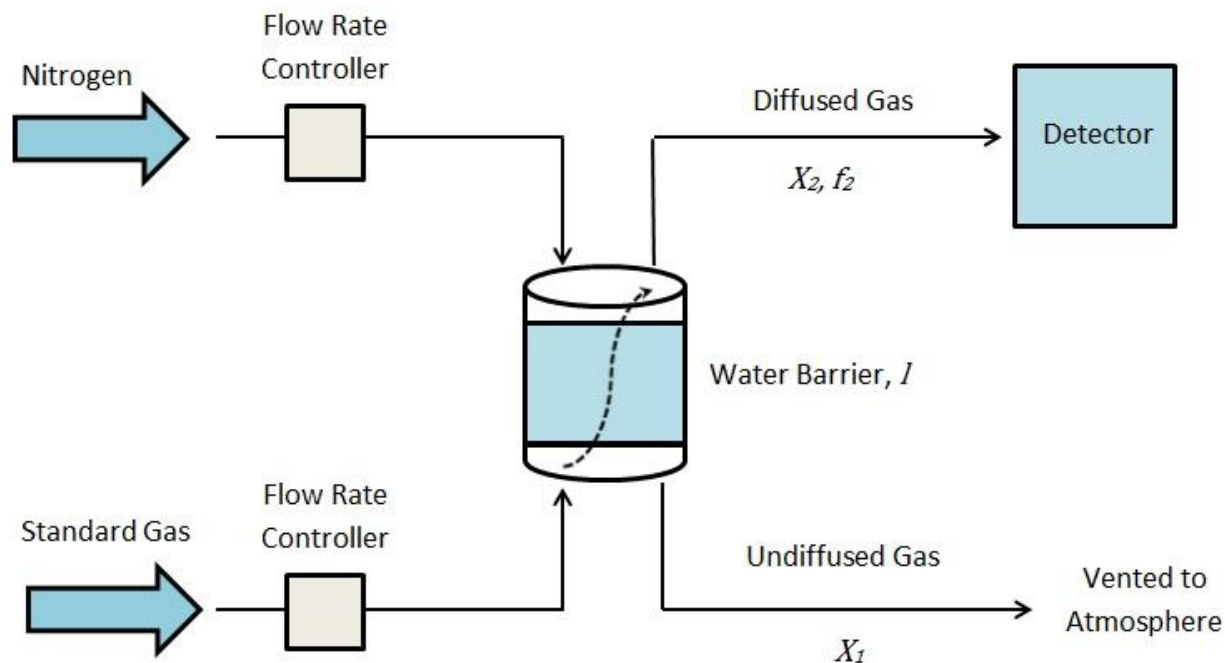


Figure 1. A schematic of the experimental method used to diffuse the standard gas across a water barrier. The CF_3SF_5 and SF_6 concentrations were monitored using gas chromatography with an electron capture detector. The concentrations were monitored until the process reached steady state.

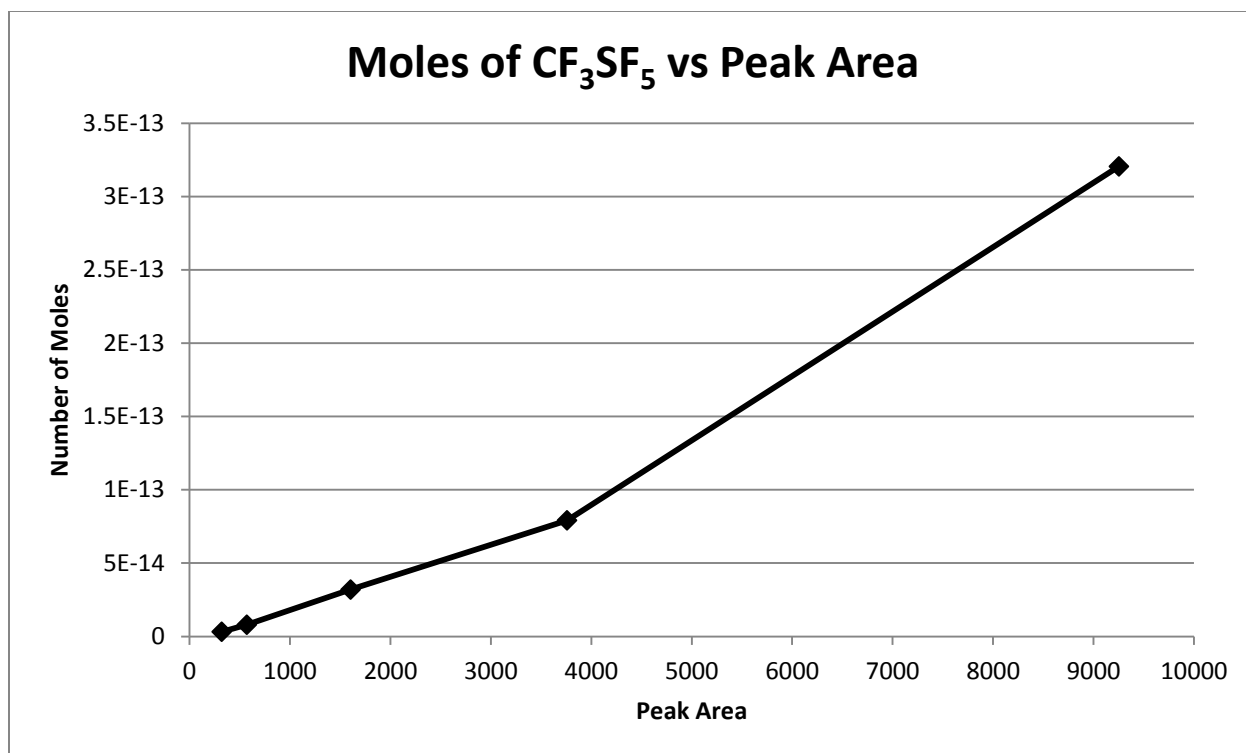


Figure 2. An example of a calibration curve used for CF_3SF_5 . The peak areas from diffusivity experiments were bracketed with known standards. A piece-wise linear fit was used to measure concentration. The majority of concentration measurements resulted in peak areas in the range of 5000-8000. The relative error for each point on the calibration curve was under 0.62%.

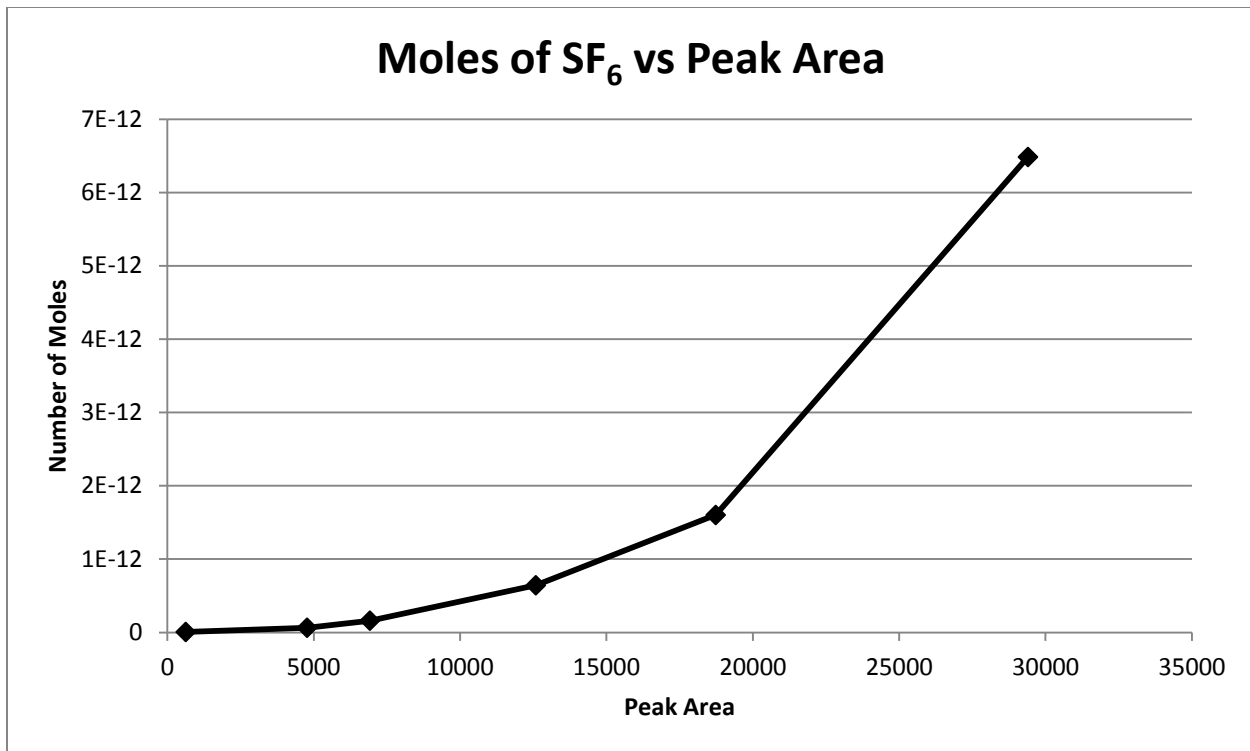


Figure 3. An example of a calibration curve used for SF₆. A piece-wise linear fit was used to measure concentration. The flow rate of nitrogen was adjusted to position the diffused gas concentration in the most linear region of the calibration curve (a peak area of 7000-12000). The dilution step positioned the diluted gas in the same region of the curve. The relative error for each point on the calibration curve was under 0.45%.

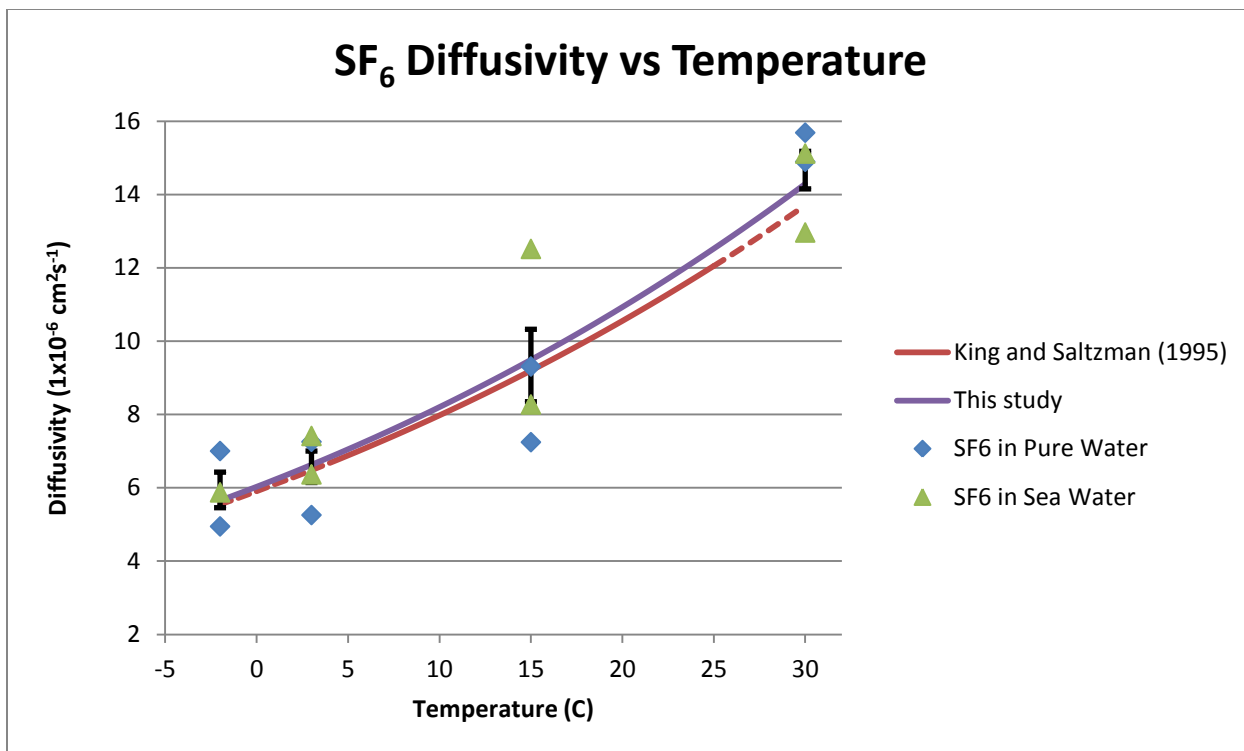


Figure 4. Diffusion coefficients for SF₆ in pure water and sea water compared to the equation of King and Saltzman (1995). The results for the pure water and seawater measurements were aggregated in the Arrhenius model. The error bars present the standard error for diffusivity at each measured temperature. The results for this experiment were in agreement with previous studies, particularly at lower temperatures. The dashed portions of the line from the King and Saltzman (1995) equation depict where the equation is extrapolated beyond the measured range. The equation for this study is: $D_{SF_6} = 0.037 \exp(-19.8/RT)$.

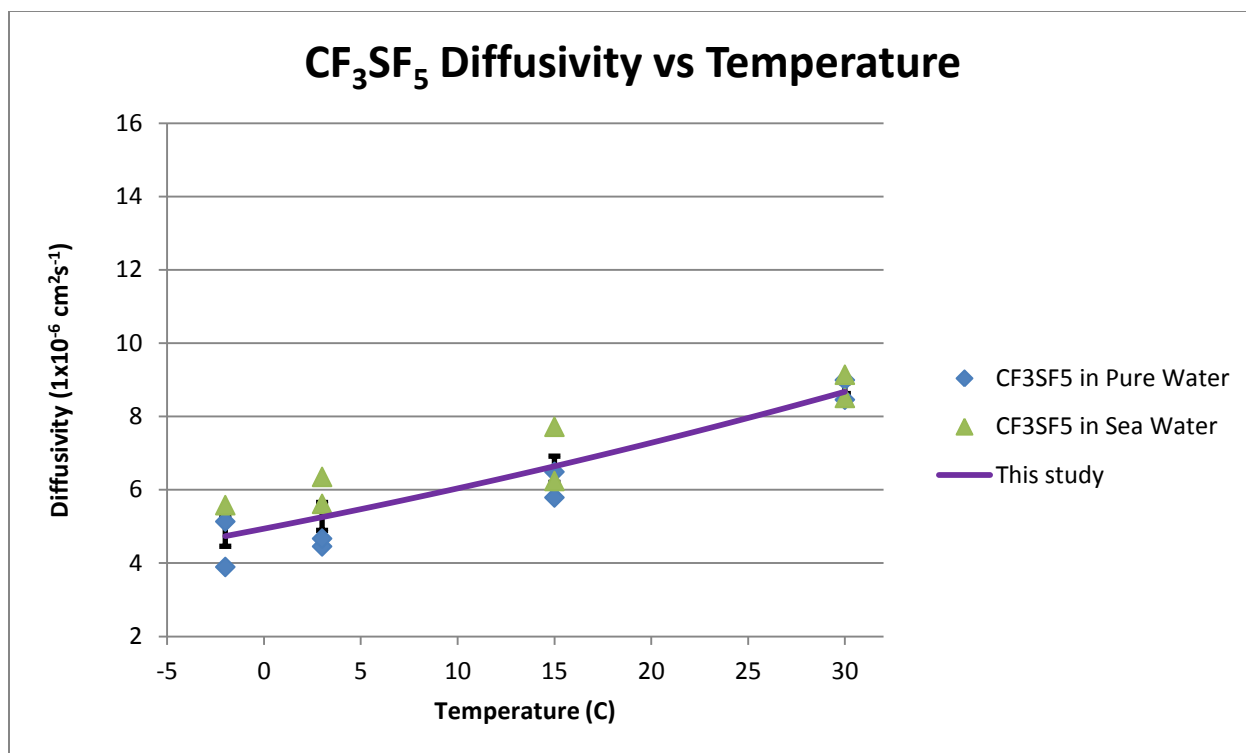


Figure 5. Diffusion coefficients of CF₃SF₅ in pure water and sea water. The results for the pure water and seawater measurements were aggregated in the Arrhenius model. The error bars present the standard error for diffusivity at each measured temperature. The CF₃SF₅ diffusion coefficients were lower than the SF₆ diffusion coefficients, as expected due to its increased molecular mass. The equation for this study is: $D_{CF_3SF_5} = 0.0015 \exp(-12.9/RT)$

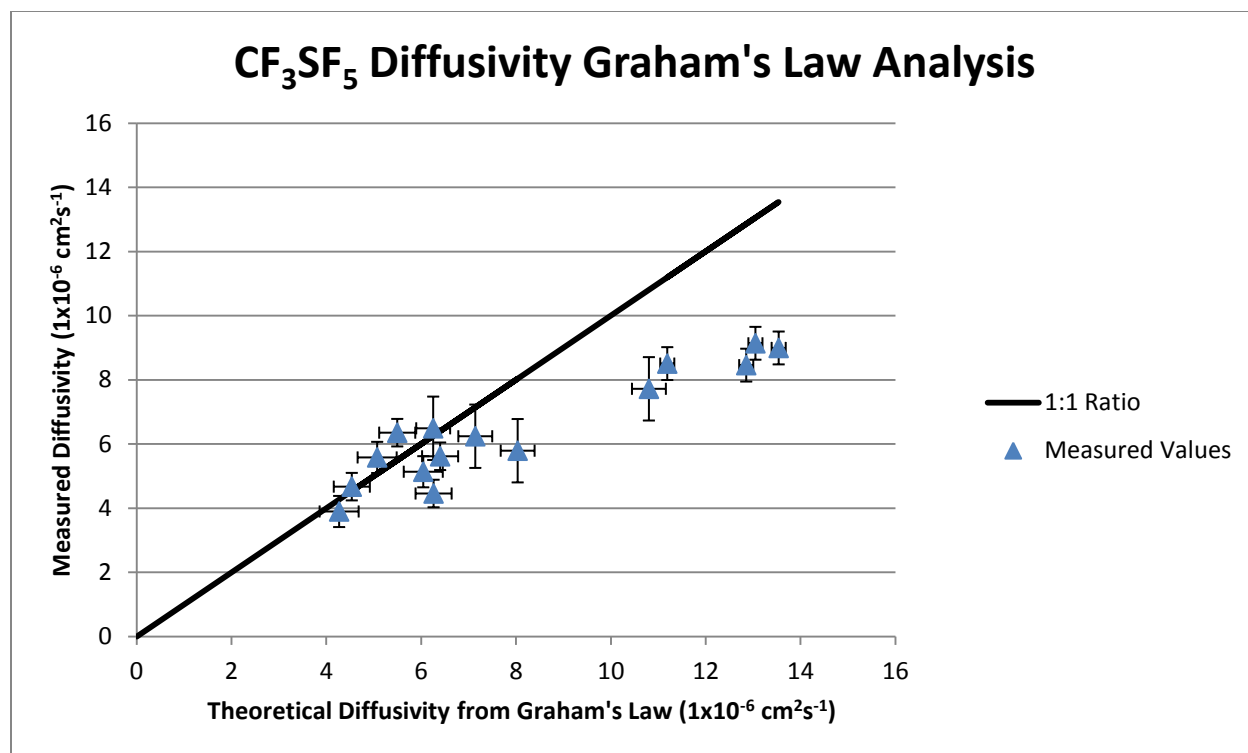


Figure 6. Measured diffusion coefficients of CF₃SF₅ compared to theoretical results from Graham's Law. The 1:1 ratio line presents the points where measured diffusivity is equal to theoretical diffusivity from Graham's Law. The vertical error bars present the error in CF₃SF₅ diffusivity measurements. The horizontal error bars present the error in SF₆ diffusivity measurements, which were used directly in the Graham's Law analysis.

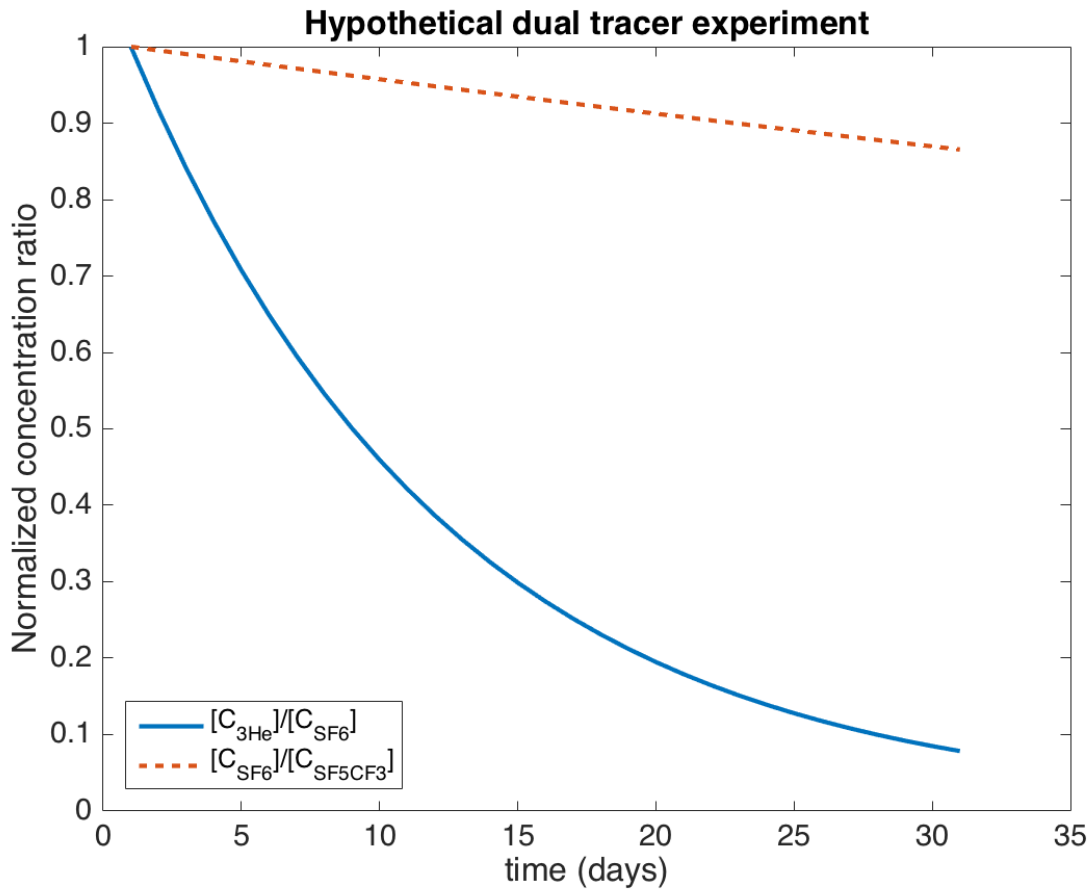


Figure 7: Normalized concentration ratio of $^3\text{He}:\text{SF}_6$ and $\text{SF}_6:\text{SF}_5\text{CF}_3$ within a hypothetical dual tracer experiment. Parameters used were a gas transfer velocity of $k_{660} = 5 \text{ m d}^{-1}$, mixed-layer depth of 50 m, water temperature of $0 \text{ }^\circ\text{C}$, and salinity of 34 g/kg. At $0 \text{ }^\circ\text{C}$, we used diffusivity values of 4.94×10^{-6} , 6.05×10^{-6} , and $4.3 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ for CF_3SF_5 , SF_6 , and ^3He , respectively.