Solubilities of chlorofluorocarbons 11 and 12 in water and seawater

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Abstract—The solubilities of dilute mixtures of the chlorofluorocarbons CCl_3F (CFC-11) and CCl_2F_2 (CFC-12) in pure water and seawater over the temperature range 0 to 40°C have been measured by gas chromatography. The data have been fitted to equations in temperature and salinity of the form used previously to fit the solubilities of other gases. The fitted values have an estimated accuracy of ~1.5% and a relative precision of ~0.7% for both chlorofluorocarbons. The nonideal behavior of these compounds in dilute air mixtures is discussed, and their solubilities from a water-saturated atmosphere are presented in parametric form.

INTRODUCTION

IN RECENT years the dissolved atmospheric chlorofluorocarbons CCl_3F (CFC-11) and CCl_2F_2 (CFC-12) have been used increasingly as tracers of oceanic circulation and mixing processes (GAMMON et al., 1982; BULLISTER and WEISS, 1983; WEISS et al., 1985). To interpret the distributions of these compounds in the oceans and in fresh waters, especially with respect to evaluating the degree of atmospheric saturation of surface waters under a wide variety of natural conditions, it is necessary to know accurately their solubilities as functions of both temperature and salinity.

Unfortunately, the CFC-11 and CFC-12 solubility data available in the literature prior to the development of these new oceanic tracer techniques provided neither the accuracy nor the range of temperatures and salinities required for this work, and several laboratories have undertaken to fill this gap. HUNTER-SMITH et al. (1983) measured the solubility of CFC-11 in water and seawater over the temperature range 5 to 33°C, and WISEGARVER and CLINE (1985) measured the solubilities of both CFC-11 and CFC-12 in seawater over the temperature range 0 to 32°C, but only at a single temperature (25°C) in water. We report here the results of our CFC-11 and CFC-12 solubility measurements, which are the first to cover the temperature range of 0 to 40°C in water and in seawater for both of these gases.

EXPERIMENTAL METHOD

Measurements of the solubilities of a number of gases in water and seawater have been made in this laboratory using a microgasometric technique (e.g. WEISS, 1971; WEISS and KYSER, 1978; WEISS and PRICE, 1980). Because this technique measures the solubility of a pure gas at a pressure of ~1 atm, there are several serious difficulties in using this

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approach to determine the solubilities of CFC-11 and CFC-12 in dilute air mixtures. At 1 atm, CFC-11 is a liquid at temperatures below 24°C. We therefore attempted to carry out microgasometric solubility measurements using a 20% mixture of CFC-11 in He which would not condense over the temperature range of our measurements, making appropriate corrections for the known solubility of the He in the mixture. Because CFC-12 has a higher vapor pressure, we could attempt the microgasometric measurements with the pure gas. However, for both gases the results were far less reproducible than our previous experiences with the microgasometric technique had led us to expect. We ascribe this poor reproducibility to the extreme nonideality of these CFC's near their condensation pressures, and to their extremely high miscibilities in greases and in other contaminants which may have been present in the microgasometric apparatus. Even if the results of the microgasometric measurements had been reproducible and unaffected by contamination, the lack of cross-virial coefficients for these CFC's in air, based either on direct measurements or on a sound theoretical treatment, would have prevented accurate calculation of the solubilities of CFC-11 and CFC-12 in dilute air mixtures from the results of these measurements.

In view of these complications, we decided instead to measure the solubilities of CFC-11 and CFC-12 by equilibrating a dilute mixture of these gases with water and seawater at various temperatures and known pressure and then measuring their concentrations in both the gas and liquid phases by gas chromatography. Our equilibration apparatus is shown schematically in Fig. 1. It contains a 1.2 l cylindrical flat-bottomed glass equilibration chamber, immersed in a constant temperature bath which is controlled to ±0.02°C. The ~0.4 l of water or seawater used in each solubility experiment is siphoned to the equilibration chamber from a glass storage carboy mounted ~1.5 m above the chamber. The gas mixture used in the equilibration is stored in an aluminium high-pressure cylinder and is supplied to the equilibration chamber through a pressure regulator and flow controller. To avoid exchange with room air, the gas mixture is exposed only to impermeable metal and glass plumbing, and prior to entering the equilibration chamber it is passed through a water bubbler to saturate it with water vapor at the temperature of the experiment. The gas effluent from the equilibration chamber is isolated from back-mixing of room air by bubbling through the outlet of a vent tube which is submerged ~1 cm below the surface of the constant temperature bath. The water inside the equilibration chamber is mixed by a glass-covered magnetic stirring bar, driven by a submersible magnetic stirring motor.

The gas mixture used in the equilibrations was prepared in our laboratory from the pure components, and contained CFC-11 and CFC-12 diluted in ultra-pure nitrogen to approximately 10 times their present atmospheric mixing ratios. This concentration range was selected to increase the chromatographic signal compared to natural samples, and also to reduce the importance of various sources of contamination and blanks. Even at these elevated concentrations, the mole fractions of both CFC's are on the order of 10^{-9}, and the mixture is still effectively at infinite dilution in the sense that a negligible fraction of the molecular interactions involves two CFC molecules. These concentrations are therefore still well within the range in which the fugacity/partial pressure ratio of each CFC is independent of concentration. Since the goal of this research is to determine the solubilities of atmospheric CFC's, it probably would have been preferable to prepare our gas mixture in synthetic air rather than in nitrogen. However, this distinction is almost certainly negligible, since the molar volumes of air and pure nitrogen over the temperature
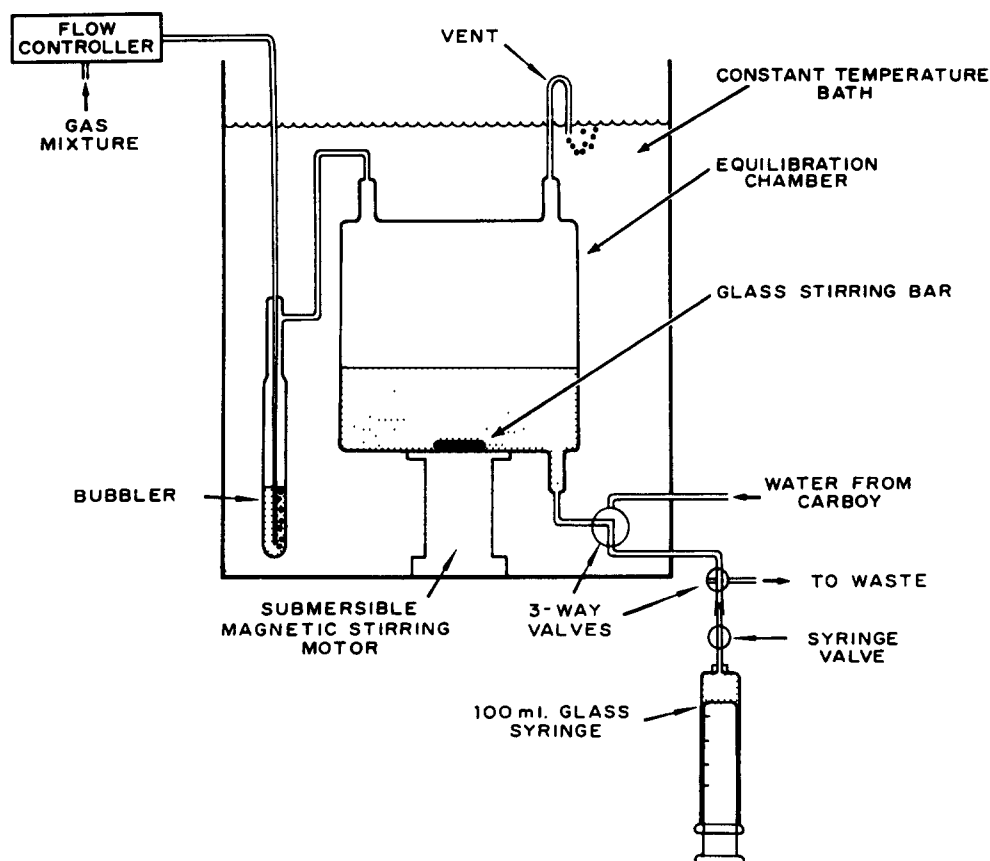
Fig. 1. Schematic diagram of the equilibration apparatus.

range of our experiments, as calculated from their second virial coefficients (SENGERS *et al.*, 1971), are nearly ideal and differ from each other by only 1 part in 10^4.

The seawater used in the experiment was surface water collected at La Jolla, evaporated to increase its salinity to $\sim$36‰, poisoned with 1 mg l^{-1} of $HgCl_2$, and passed through a 0.45 μm filter to remove particulates. This seawater was stored in a large glass carboy, in which the air space was vented to the atmosphere through a 6 m length of 2 mm i.d. Nylon tubing to minimize evaporative loss during the course of the experiments. The salinity of this seawater, measured 3 times over this period, was 35.807 ± 0.006‰. The pure water used in the experiment was deionized and stored in a similar carboy.

The kinetics of the saturation experiment were measured for water and for seawater over the 0 to 40°C temperature ranges by substituting CFC-free nitrogen for the gas mixture and monitoring the removal of dissolved CFC-11 and CFC-12 which were originally in approximate equilibrium with laboratory air. The results demonstrate, as expected, that the exchange process is first order for both gases, with the e-folding exchange time τ being approximately equal for both gases and ranging from about 120 min at 0°C to about 20 min at 40°C in both water and seawater.

Using these exchange times, the solubility experiments were run for periods of at least 8 τ. During the experiment the flow rate of the gas mixture through the gas space in the

equilibration chamber was maintained at a value between 24 and 32 ml min^{-1}. We have solved the differential equation relating the gas flow rate, the value of τ, the volumes of water and gas in the system, and the value of the solubility coefficient, to the degree of saturation expected at the end of each experiment. According to this calculation, the water in all of our experiments was saturated to within 0.05% of equilibration. As an additional precaution, the stirring rate in the chamber was increased during the first 2 to 4 τ of each experiment, and was then reduced to the normal rate to avoid possible entrainment of bubbles which might lead to oversaturation. Also, the tubing leading from the bottom of the chamber was flushed during the experiment by draining about 5 ml of water at 1 τ intervals.

The barometric pressure was measured to ±0.0001 atm at the beginning and end of each experiment using a precision aneroid barometer, and the pressure of the equilibration chamber was calculated by adding the 0.001 atm hydrostatic pressure produced by the submerged vent tube. In some cases the barometric pressure varied by as much as 0.005 atm over the length of the experiment. The mean equilibration pressure of the experiment was taken as the linearly interpolated pressure 2 τ before the end of the experiment.

Following the procedures developed for our shipboard dissolved CFC measurements (BULLISTER, 1984; WEISS et al., 1985), samples of equilibrated water were transferred to the gas chromatographic extraction and analysis system using 100 ml precision-ground glass syringes. The syringes were filled through a short length of flexible 2 mm i.d. Nylon tubing, attached to the equilibration chamber through a series of valves designed to allow flushing with at least 100 ml of equilibrated water and the removal of all traces of bubbles. Independent tests using CFC-free water showed that samples could be transferred through this tubing without significant exchange of CFC-11 or CFC-12 with the surrounding air or water bath.

The syringes were transferred rapidly to the extraction system, where samples of ~30 ml were injected into the stripping chamber. The dissolved CFC's were then purged by a stream of purified argon–methane carrier gas and collected on a –30°C Porasil C and Porapak T trap for injection into the gas chromatograph. Impurities with long elution times were removed by standard precolumn techniques. The CFC-11 and CFC-12 peaks were separated using a Porasil C column and detected by a Shimadzu [63]Ni electron-capture detector operating in constant current mode. Peak areas were determined by a Spectra Physics SP4100 digital integrator which also provided precisely timed automatic control of sample injection and precolumn backflushing valves. The design and operation of the gas chromatographic extraction and analysis system are described in detail by BULLISTER (1984).

To assure complete extraction of dissolved CFC's, samples were restripped and reanalyzed before being drained from the stripping chamber. As the shipboard measurements had already demonstrated (BULLISTER, 1984), seawater samples are stripped at close to their theoretical first-order stripping efficiency, and the amount of dissolved CFC-11 and CFC-12 removed by restripping is negligible. However, with fresh water samples the bubbles formed in the stripper are much larger and the consequent reduction in bubble surface area greatly reduces the stripping efficiency. Restripping of these samples was necessary, as opposed to lengthening the original stripping time, because of the risk with extended stripping times of CFC loss through the low temperature trap.

The gas mixture used in the equilibrations was also used in place of the calibration

standard gas in the gas chromatograph. Known volumes of the dry gas mixture were injected at measured temperature and barometric pressure by means of two gas sample valves with 3 and 0.7 ml sample loops, and the CFC's were collected on the same low-temperature trap used in the water sample measurements. By analyzing various multiple aliquots of the gas mixture collected together on the trap, the non-linearities of the instrument were determined over a range of CFC amounts which bracketed the peak areas obtained from the water samples. The response of the instrument for both CFC's was found to be well-represented by an equation of the form

$$\frac{n}{A} = \frac{a_1 A + a_2}{a_3 A + 1},$$
(1)

where n is the number of moles of the gas mixture injected, A is the peak area, and the a's are constants. This equation was fitted to the results of the gas mixture analyses for each CFC by an iterative least-squares technique.

It is important to recognize that the measurement of gas solubility requires the accurate determination of the concentration ratio between the gas and liquid phases under known equilibrium conditions. Thus, by using the equilibration gas mixture to characterize the response of the gas chromatograph, the measurement becomes independent of the absolute calibration of this mixture. However, the accuracy of the solubility measurement does depend directly on the ratio of the volume of gas mixture analyzed to the volume of liquid analyzed. The volume of the gas sample loops were determined gravimetrically to $\pm 0.1\%$ by filling with degassed water. The volume of equilibrated water injected into the extraction system was determined to $\pm 0.3\%$ by measuring the syringe travel and plunger diameter with a precision dial caliper. The volume of water sampled is also temperature dependent, and we have determined from measurements of temperature changes in the syringes that the error in the volume introduced by assuming that the injection temperature is the same as the equilibration temperature is $<0.05\%$.

There are several additional sources of potential error. The gas mixture entering the equilibration chamber was passed through a bubbler containing pure water. In the seawater saturation experiments this resulted in a net flux of water into the equilibration chamber given by the gas flux times the water vapor pressure difference between water and seawater. We calculate that this effect would produce a completely negligible increase in the measured solubility of $<0.001\%$. There was also a potential for contamination of samples during transfer from the equilibration chamber to the extraction apparatus which we measured periodically by transferring samples of CFC-free water. Since we believe this contamination to have been produced by entrapment of minute amounts of contaminated room air, it was subtracted as a sampling blank which ranged for 0.1 to 2% of the CFC's in our gas-mixture equilibrated samples.

RESULTS AND DISCUSSION

According to the modified form of Henry's law for real gases (WEISS, 1974; WEISS and PRICE, 1980) the solubilities of CFC-11 and CFC-12 may be expressed in terms of the equation

$$C^* = K_0 f \exp\left[(1-P)\bar{v}/RT\right],$$
(2)

where C^* is the equilibrium concentration of the dissolved CFC in volumetric (mol l^{-1}) or

gravimetric (mol kg^{-1}) units, f is the fugacity of the CFC in atm, K_0 is the fugacity equilibrium constant in either mol l^{-1} atm^{-1} or mol kg^{-1} atm^{-1}, depending on the concentration units, P is the total pressure in atm, $\bar{v}$ is the partial molal volume, R is the gas constant (82.056 cm^3 atm mol^{-1} K^{-1}), and T is the absolute temperature. Although values of $\bar{v}$ have not been measured directly, the empirical relationship of Moore et al. (1982, equation 7) predicts values of 77 cm^3 mol^{-1} for CFC-11 and 69 cm^3 mol^{-1} for CFC-12. Thus, compared to the precision of our CFC solubility measurements, the exponential term in equation (2) can be neglected for values of P within $\sim$0.3 atm of 1 atm.

As noted above, the difficulty with using equation (2) to report the results of our CFC solubility measurements lies in the lack of adequate data on the cross-virial coefficients needed to evaluate the fugacities of CFC-11 and CFC-12 in dilute air or nitrogen mixtures. For these mixtures at total pressures near 1 atm we define the partial pressure equilibrium constant K' by the relation

$$\frac{K'}{K_0} = \frac{f}{x'(P - p_{H_2O})},\tag{3}$$

where x' is the dry air mole fraction of the CFC, p_{H_2O} is the water vapor pressure in atm, and the right-hand side of the equation is the fugacity/partial pressure ratio of the CFC in the mixture. Substituting into equation (2) and neglecting the exponential term we obtain the equation

$$C^* = K'x'(P - p_{H_2O})\tag{4}$$

which is valid only for $x' \ll 1$ and total pressures near 1 atm, but avoids the need to evaluate the nonideality of the CFC in the mixture. As with K_0, the constant K' may be in either mol l^{-1} atm^{-1} or mol kg^{-1} atm^{-1}, depending on the units of the concentration. Similarly, a Bunsen coefficient β' for the CFC's in dilute air or nitrogen mixture may be defined as the equal to $K'V^\dagger$, where K' is in volumetric units and $V^\dagger$ is the volume of one mole of the gas mixture at STP.

We have calculated values of K' from our measurements by first converting the peak areas of the CFC's extracted from the equilibrated samples to an equivalent number of moles n of the equilibration gas mixture using equation (1). Values of n from multiple stripping of the sample were combined, and the appropriate blanks were subtracted. Then K' was calculated according to the equation

$$K' = \frac{n}{V_w(P - p_{H_2O})},\tag{5}$$

where V_w is the measured volume of the water sample and K' is in mol l^{-1} atm^{-1}. In these calculations we have used the temperature and salinity dependence of p_{H_2O} as formulated by Weiss and Price (1980).

The experimental values of K' for CFC-11 and CFC-12 are listed in Table 1 together with the temperatures and salinities at which they were measured. At each temperature and salinity, a Q test at the 90% confidence level (Dean and Dixon, 1951) was performed on the data. In cases of small temperature differences within a group of measurements, the slope of the temperature dependence was used to normalize the data to a single temperature before the Q test was applied. This resulted in the rejection of the 5 CFC-11

Table 1. *Experimental CFC-11 and CFC-12 solubilities in volumetric units of* K' (mol l^{-1} atm ^{1})

S = 0‰			S = 35.807‰		
t (°C)	CFC-11 10² K'	CFC-12 10³ K'	t (°C)	CFC-11 10² K'	CFC-12 10³ K'
0.85	3.7221	9.015	−0.77	2.8152	6.708
0.85	3.6555	9.122	−0.77	2.7588	6.931*
0.85	3.6636	8.871	−0.52	2.7263	6.672
0.85	3.6818	8.926	−0.52	2.6985	6.646
0.85	3.6561	8.998	−0.45	2.7107	6.638
0.85	3.6371	9.047	−0.43	2.7065	6.526
9.58	2.1092	5.532	−0.37	2.7110	6.637
9.59	2.1600	5.519	−0.37	2.7056	6.611
9.59	2.1532	5.672	4.79	1.9706	4.905
9.59	2.1498	5.504	4.79	1.9446	4.960
9.59	2.1760	5.650	4.79	1.9601	4.803
9.59	2.1647	5.558	4.79	1.9607	4.975
19.82	1.2561'	3.347'	4.81	1.8770*	4.887
19.87	1.2646	3.396'	4.82	1.9773	4.973
19.89	1.2756	3.461	4.84	1.9318	5.022
19.89	1.2707	3.450	9.19	1.5302	4.020
19.92	1.2785	3.510	9.19	1.5293	3.978
19.93	1.2785	3.530	9.19	1.5330	4.008
29.87	0.8697	2.480	9.19	1.5372	4.029
29.87	0.8783	2.508	9.19	1.5727*	3.972
29.87	0.8715	2.601*	9.19	1 5404	4.002
29.89	0.8712	2.519	20.43	0.8648*	2.427
29.89	0.8645	2.494	20.44	0.8868	2.553*
31.50	0.8223	2.433	20.44	0.8792	2.463
31.79	0.8366	2.361	20.44	0.8749	2.465
31.79	0.8314	2.363	20.44	0.8788	2.453
31.79	0.8543'	2.394	20.44	0 8780	2.470
31.89	0.8222	2.341	29.53	0.6085	1.754
31.89	0.8129	2.338	29.53	0.6031	1.738
31.89	0.8240	2.354	29.55	0.6182*	1.732
31.89	0.8263	2.338	29.55	0.6042	1.770
40.73	0.6180	1.830	29.55	0.6037	1.750
40.73	0 6282'	1.873	29.55	0.6020	1.753
40.73	0.5979	1.805	39 90	0.4280	1.318
40.73	0.6130	1.832	39.91	0.4301	1.322
40.76	0.6048	1.813	39.93	0.4299	1.303
40 80	0.6060	1.803	39.93	0.4357*	1.367'
			39.93	0.4281	1.282

* Rejected by *Q* test.
' Rejected by curve fitting.

points and 3 CFC-12 points indicated in Table 1. The remaining data were then fitted by least-squares to an equation in temperature and salinity which has been used to fit the solubilities of many other gases. This equation is derived from the integrated van't Hoff equation and the logarithmic Setchénow salinity dependence, and has the form (WEISS, 1970, 1974)

$$\ln K' = a_1 + a_2(100/T) + a_3 \ln (T/100)$$
$$+ S[b_1 + b_2(T/100) + b_3(T/100)^2], \tag{6}$$

where K' may be expressed either in mol l^{-1} atm^{-1} or mol kg^{-1} atm^{-1}, T is the absolute

temperature, S is the salinity in parts per thousand (‰), and the a's and b's are constants. During the curve fitting procedures, values which deviated from the curve by more than 2.7 times the standard error were iteratively rejected. This resulted in the removal of three additional points for each CFC as indicated in Table 1.

The constants obtained by fitting the CFC-11 and CFC-12 K' data to equation (6) in both volumetric and gravimetric units are given in Table 2. Figure 2 and Fig. 3 show the deviations of the measured volumetric data from the fits to equation (6) for CFC-11 and CFC-12, respectively. These deviations are plotted in units of $10^2 \Delta \ln K'$ so that the ordinates represent percentage deviations of the fitted points from the curves. The standard errors of the points about the fitted curves are 1.06% for CFC-11 and 1.26% for

Table 2.   Constants for the calculation of the solubility coefficient K' of CFC-11 and CFC-12 in volumetric and gravimetric units as given by equation (6)

| | K' (mol l^{-1} atm^{-1}) | | K' (mol kg^{-1} atm^{-1}) | |
	CFC-11	CFC-12	CFC-11	CFC-12
a_1	−134.1536	−122.3246	−136.2685	−124.4395
a_2	203.2156	182.5306	206.1150	185.4299
a_3	56.2320	50.5898	57.2805	51.6383
b_1	−0.144449	−0.145633	−0.148598	−0.149779
b_2	0.092952	0.092509	0.095114	0.094668
b_3	−0.0159977	−0.0156627	−0.0163396	−0.0160043

Fig. 2.   Deviations of the experimental CFC-11 solubility data in volumetric units from the fit to equation (6), plotted against temperature. The pure water measurements are shown as filled circles and the seawater measurements are shown as filled triangles. The plotted values of $10^2 \Delta \ln K'$ represent percentage deviations from the fitted curve, and the dashed horizontal lines show ±1 S.E. of 1.06%. The results of HUNTER-SMITH *et al.* (1983) and WISEGARVER and CLINE (1985) are plotted for comparison.
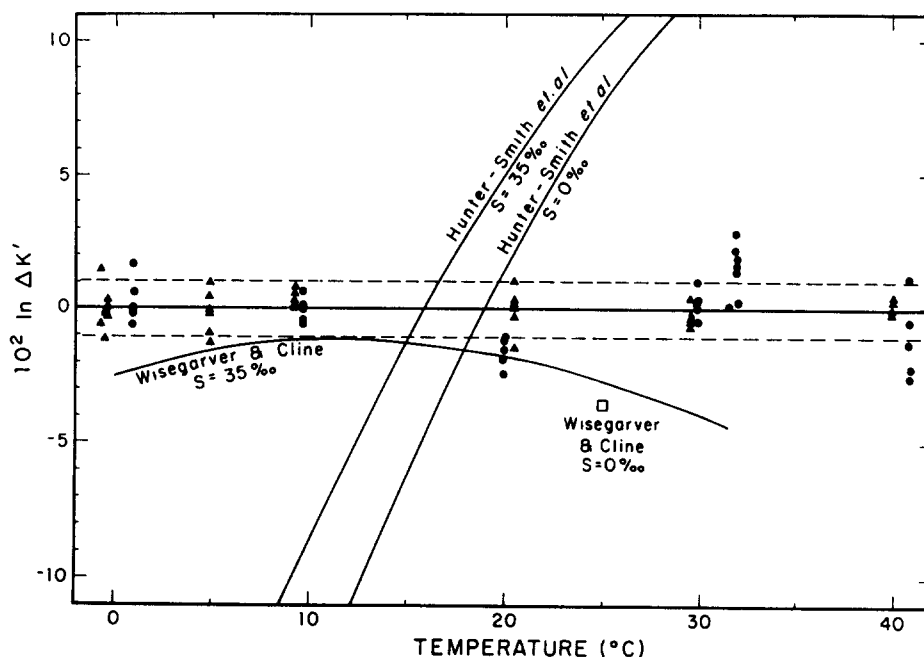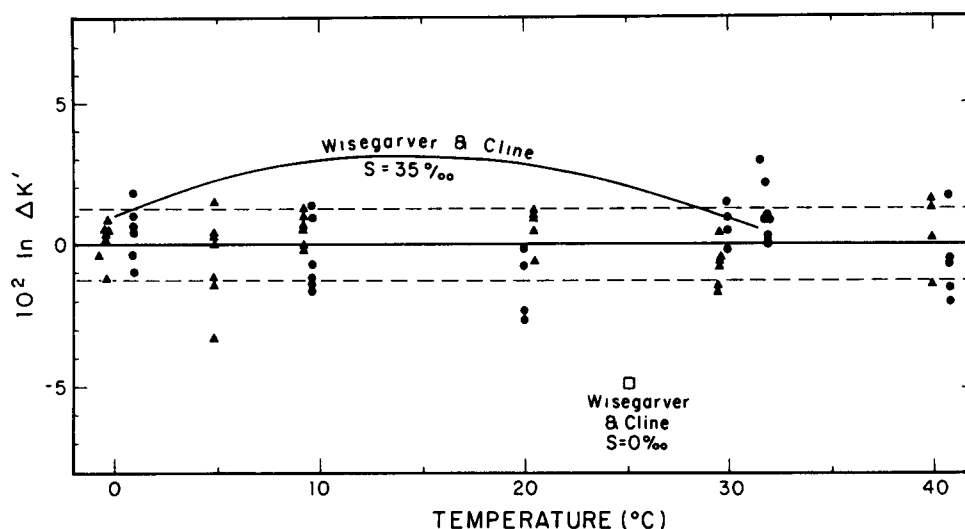
Fig. 3. Deviations of the experimental CFC-12 solubility data in volumetric units from the fit to equation (6), plotted against temperature. The pure water measurements are shown as filled circles and the seawater measurements are shown as filled triangles. The plotted values of $10^2 \Delta \ln K'$ represent percentage deviations from the fitted curve, and the dashed horizontal lines show ± 1 S.E. of 1.26%. The results of WISEGARVER and CLINE (1985) are plotted for comparison.

Table 3. Values of K' in gravimetric units (10^{-2} mol kg^{-1} atm^{-1}) for CFC-11

t (°C)	Salinity (‰)								
	0	10	20	30	34	35	36	38	40
−1	–	–	3.338	2.998	2.871	2.840	2.810	2.750	2.692
0	3.871	3.478	3.125	2.808	2.690	2.661	2.633	2.577	2.523
1	3.624	3.258	2.929	2.633	2.523	2.497	2.470	2.418	2.367
2	3.397	3.056	2.749	2.472	2.370	2.345	2.320	2.271	2.224
3	3.188	2.869	2.582	2.324	2.228	2.204	2.181	2.136	2.091
4	2.996	2.697	2.429	2.187	2.097	2.075	2.053	2.010	1.969
5	2.818	2.539	2.287	2.060	1.975	1.955	1.934	1.894	1.855
6	2.655	2.392	2.155	1.942	1.863	1.844	1.825	1.787	1.750
8	2.363	2.131	1.922	1.733	1.663	1.645	1.628	1.595	1.562
10	2.113	1.907	1.720	1.552	1.490	1.474	1.459	1.430	1.400
12	1.898	1.713	1.547	1.396	1.340	1.326	1.313	1.286	1.260
14	1.712	1.546	1.396	1.260	1.210	1.198	1.186	1.162	1.138
16	1.551	1.401	1.265	1.142	1.097	1.086	1.075	1.053	1.032
18	1.410	1.274	1.151	1.039	0.998	0.988	0.978	0.958	0.939
20	1.288	1.163	1.051	0.949	0.911	0.902	0.893	0.875	0.857
22	1.181	1.066	0.963	0.869	0.834	0.826	0.818	0.801	0.785
24	1.086	0.981	0.885	0.799	0.767	0.759	0.751	0.736	0.721
26	1.003	0.905	0.817	0.737	0.707	0.700	0.693	0.679	0.665
28	0.930	0.839	0.756	0.682	0.654	0.647	0.641	0.628	0.615
30	0.865	0.780	0.702	0.633	0.607	0.601	0.595	0.582	0.570
32	0.807	0.727	0.654	0.589	0.565	0.559	0.553	0.542	0.530
34	0.756	0.680	0.612	0.550	0.527	0.522	0.516	0.505	0 495
36	0.710	0.638	0.573	0.515	0.494	0.488	0.483	0.473	0.463
38	0.670	0.601	0.539	0.484	0.463	0.458	0.453	0.444	0.434
40	0.633	0.567	0.508	0.455	0.436	0.431	0.426	0.417	0.408

CFC-12. Values of K' in gravimetric units obtained from these curves at various temperatures and salinities are listed in Tables 3 and 4 for CFC-11 and CFC-12, respectively.

We have also expressed our results in terms of the solubility function F, defined by WEISS and PRICE (1980) for the solubility of an atmospheric trace constituent with $x' \ll 1$ in *moist* air at the water-saturated interface, by the expression

$$C^* = x'F. \tag{7}$$

From this expression and equation (4), we obtain the relation

$$F = K'(P - p_{H_2O}) \tag{8}$$

which, because of the limitations of K', is valid only at total pressures near 1 atm.

To facilitate the use of our CFC-11 and CFC-12 solubility data, we have calculated the function F at a total pressure of 1 atm as represented by a polynomial of the form (WEISS and PRICE, 1980)

$$\ln F = a_1 + a_2(100/T) + a_3 \ln (T/100) + a_4(T/100)^2$$
$$+ S[b_1 + b_2(T/100) + b_3(T/100)^2], \tag{9}$$

which is similar to the form of equation (6), except that the additional T^2 term is required to fit the effect of water vapor. The constants for this equation were easily calculated by fitting $\ln(1 - p_{H_2O})$ to the right-hand side of the equation and adding the constants for each

Table 4. *Values of* K' *in gravimetric units* $(10^{-3}$ mol kg^{-1} atm$^{-1})$ *for CFC-12*

t (°C)	Salinity (‰)								
	0	10	20	30	34	35	36	38	40
−1	–	–	8.079	7.261	6.958	6.884	6.811	6.667	6.526
0	9.420	8.472	7.620	6.853	6.569	6.499	6.431	6.296	6.164
1	8.881	7.993	7.194	6.475	6.208	6.143	6.078	5.952	5.827
2	8.382	7.549	6.799	6.123	5.872	5.811	5.751	5.632	5.515
3	7.920	7.137	6.432	5.797	5.561	5.503	5.446	5.334	5.224
4	7.491	6.755	6.092	5.493	5.271	5.217	5.163	5.057	4.954
5	7.093	6.400	5.775	5.211	5.001	4.950	4.899	4.799	4.702
6	6.724	6.070	5.480	4.947	4.749	4.701	4.653	4.559	4.467
8	6.060	5.477	4.949	4.473	4.295	4.252	4.209	4.125	4.042
10	5.485	4.961	4.487	4.058	3.899	3.860	3.821	3.745	3.671
12	4.983	4.511	4.083	3.696	3.551	3.516	3.481	3.412	3.345
14	4.545	4.117	3.729	3.377	3.246	3.214	3.182	3.120	3.059
16	4.161	3.771	3.417	3.096	2.977	2.947	2.918	2.862	2.806
18	3.824	3.466	3.142	2.848	2.739	2.712	2.685	2.633	2.582
20	3.526	3.197	2.899	2.628	2.527	2.503	2.478	2.430	2.383
22	3.263	2.959	2.683	2.433	2.340	2.317	2.294	2.250	2.206
24	3.030	2.748	2.491	2.259	2.172	2.151	2.130	2.089	2.048
26	2.823	2.559	2.320	2.104	2.023	2.003	1.984	1.945	1.907
28	2.639	2.391	2.168	1.965	1.889	1.870	1.852	1.816	1.781
30	2.474	2.241	2.031	1.840	1.769	1.751	1.734	1.700	1.667
32	2.327	2.107	1.908	1.728	1.660	1.644	1.628	1.596	1.564
34	2.195	1.986	1.797	1.626	1.563	1.547	1.532	1.501	1.472
36	2.077	1.878	1.698	1.535	1.474	1.460	1.445	1.416	1.388
38	1.970	1.780	1.608	1.452	1.395	1.380	1.367	1.339	1.312
40	1.875	1.692	1.527	1.378	1.322	1.309	1.295	1.269	1.243

term to those obtained by fitting ln K' to equation (6). The resulting constants for calculation of F in volumetric (mol 1^{-1} atm^{-1}) and gravimetric (mol kg^{-1} atm^{-1}) units for both CFC-11 and CFC-12 are given in Table 5. Values of F in gravimetric units obtained from these curves at various temperatures and salinities are listed in Tables 6 and 7 for CFC-11 and CFC-12, respectively.

In Figs 2 and 3 the results of the recent studies of HUNTER-SMITH *et al.* (1983) and WISEGARVER and CLINE (1985) are compared to our results. The Henry's law constant, H, used by Hunter-Smith *et al.* to report their CFC-11 solubility results, is in fact the reciprocal of the Ostwald solubility coefficient L' for dilute mixtures in nitrogen (P. S. LISS, personal

Table 5.   Constants for the calculation of the function F for CFC-11 and CFC-12 in moist air at a total pressure of 1 atm, in volumetric and gravimetric units as given by equation (9)

| | F (mol 1^{-1} atm^{-1}) | | F (mol kg^{-1} atm^{-1}) | |
	CFC-11	CFC-12	CFC-11	CFC-12
a_1	−229.9261	−218.0971	−232.0411	−220.2120
a_2	319.6552	298.9702	322.5546	301.8695
a_3	119.4471	113.8049	120.4956	114.8533
a_4	−1.39165	−1.39165	−1.39165	−1.39165
b_1	−0.142382	−0.143566	−0.146531	−0.147718
b_2	0.091459	0.091015	0.093621	0.093175
b_3	−0.0157274	−0.0153924	−0.0160693	−0.0157340

Table 6.   The function F in gravimetric units (10^{-2} mol kg^{-1} atm^{-1}) for CFC-11 in moist air at a total pressure of 1 atm

| t (°C) | Salinity (‰) | | | | | | | | |
	0	10	20	30	34	35	36	38	40
−1	–	–	3.322	2.983	2.858	2.827	2.797	2.737	2.679
0	3.849	3.459	3.108	2.793	2.676	2.647	2.619	2.563	2.509
1	3.602	3.238	2.911	2.617	2.508	2.481	2.455	2.404	2.353
2	3.374	3.035	2.730	2.456	2.354	2.329	2.304	2.256	2.209
3	3.164	2.848	2.563	2.307	2.211	2.188	2.165	2.120	2.076
4	2.971	2.675	2.409	2.169	2.080	2.058	2.037	1.994	1.953
5	2.794	2.516	2.267	2.042	1.958	1.938	1.918	1.878	1.839
6	2.629	2.370	2.135	1.924	1.846	1.827	1.808	1.771	1.734
8	2.338	2.108	1.901	1.714	1.645	1.628	1.611	1.578	1.546
10	2.087	1.883	1.699	1.533	1.472	1.457	1.442	1.412	1.384
12	1.872	1.689	1.525	1.377	1.322	1.308	1.295	1.269	1.243
14	1.685	1.522	1.374	1.241	1.191	1.179	1.167	1.144	1.121
16	1.523	1.376	1.243	1.122	1.078	1.067	1.056	1.035	1.014
18	1.382	1.248	1.128	1.019	0.978	0.968	0.958	0.939	0.920
20	1.259	1.137	1.027	0.927	0.890	0.881	0.873	0.855	0.838
22	1.150	1.039	0.938	0.847	0.813	0.805	0.797	0.781	0.765
24	1.055	0.952	0.860	0.776	0.745	0.737	0.730	0.715	0.701
26	0.970	0.876	0.790	0.713	0.684	0.677	0.670	0.657	0.643
28	0.895	0.808	0.728	0.657	0.630	0.624	0.617	0.605	0.592
30	0.829	0.747	0.673	0.607	0.582	0.576	0.570	0.558	0.547
32	0.770	0.693	0.624	0.562	0.539	0.533	0.528	0.517	0.506
34	0.716	0.645	0.580	0.522	0.500	0.495	0.490	0.479	0.469
36	0.669	0.601	0.540	0.485	0.465	0.460	0.455	0.446	0.436
38	0.626	0.562	0.504	0.453	0.433	0.429	0.424	0.415	0.406
40	0.587	0.526	0.472	0.423	0.405	0.400	0.396	0.387	0.379

Table 7. The function F in gravimetric units (10^{-3} mol kg^{-1} atm^{-1}) for CFC-12 in moist air at a total pressure of 1 atm

t (°C)	Salinity (‰)								
	0	10	20	30	34	35	36	38	40
−1	–	–	8.039	7.225	6.923	6.849	6.777	6.634	6.493
0	9.367	8.424	7.577	6.815	6.532	6.463	6.394	6.260	6.129
1	8.825	7.943	7.149	6.434	6.169	6.104	6.040	5.914	5.791
2	8.324	7.497	6.752	6.081	5.832	5.771	5.711	5.593	5.477
3	7.860	7.084	6.384	5.753	5.519	5.462	5.405	5.294	5.185
4	7.430	6.700	6.042	5.448	5.228	5.174	5.121	5.016	4.913
5	7.031	6.344	5.724	5.165	4.957	4.906	4.856	4.757	4.660
6	6.660	6.013	5.428	4.901	4.704	4.656	4.609	4.516	4.424
8	5.995	5.418	4.896	4.424	4.249	4.206	4.164	4.080	3.998
10	5.417	4.900	4.432	4.009	3.851	3.812	3.774	3.699	3.626
12	4.914	4.448	4.026	3.644	3.502	3.467	3.433	3.365	3.299
14	4.474	4.052	3.670	3.324	3.195	3.163	3.132	3.071	3.011
16	4.087	3.704	3.356	3.041	2.924	2.895	2.867	2.811	2.756
18	3.747	3.396	3.079	2.791	2.684	2.657	2.632	2.580	2.530
20	3.446	3.124	2.833	2.569	2.470	2.446	2.422	2.375	2.329
22	3.179	2.883	2.614	2.371	2.280	2.258	2.236	2.192	2.150
24	2.942	2.668	2.419	2.194	2.110	2.089	2.069	2.029	1.989
26	2.730	2.475	2.244	2.035	1.957	1.938	1.919	1.882	1.845
28	2.540	2.303	2.088	1.892	1.820	1.802	1.784	1.749	1.715
30	2.370	2.148	1.946	1.764	1.696	1.679	1.662	1.630	1.598
32	2.217	2.008	1.819	1.647	1.583	1.568	1.552	1.522	1.492
34	2.079	1.882	1.704	1.542	1.482	1.467	1.452	1.424	1.396
36	1.955	1.768	1.599	1.446	1.389	1.375	1.362	1.334	1.308
38	1.841	1.664	1.504	1.359	1.305	1.292	1.279	1.253	1.228
40	1.738	1.569	1.417	1.279	1.228	1.215	1.203	1.178	1.155

communication), which is related to our K' by the expression

$$K' = L'/RT. \tag{10}$$

Wisegarver and Cline reported their measured solubilities in units of β', but due to the omission of a temperature term in their equation (1), they are actually in units of L' (D. WISEGARVER, personal communication). When all the results are corrected to the same units, the Hunter-Smith *et al.* CFC-11 results range from 24% below our values at 5°C in pure water to 15% above our values at 33°C in seawater. The corrected Wisegarver and Cline seawater results are in much closer agreement, with their CFC-11 values being about 1 to 4% below ours and their CFC-12 values being about 1 to 3% above ours.

The new measurements reported here greatly improve our knowledge of the solubilities of atmospheric CFC-11 and CFC-12 in water and seawater. They provide, for the first time, functions which accurately represent the solubilities of both of these gases over a broad range of temperatures and salinities encountered in natural waters. These fitted values have an estimated accuracy of about 1.5% and a relative precision (± 1 S.D.) of about 0.7% over the entire range of temperatures and salinities covered by the measurements.

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