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Henry's Law Constants and Distribution Coefficients of Sulfur Hexafluoride in Water from 25 °C to 230 °C

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The solubility of SF_6 in water has been measured between 75 °C and 230 °C by direct sampling of SF_6-saturated water contained in a stainless steel autoclave. The solubility (reported as a distribution coefficient) ranges from $\ln B = 13.93$ at 75 °C to $\ln B = 8.34$ at 230 °C. The experimental data were combined with low-temperature data from the literature to obtain an empirical equation for the Henry's law coefficient over the temperature interval 25 °C to 230 °C. At temperatures above about 210 °C an unexpectedly rapid decrease in SF_6 gas partial pressure occurred, and above this temperature deviation from Henry's law also was observed.

Introduction

The use of SF_6 as a conservative groundwater and geothermal tracer for delineating hydrogeologic parameters has been well documented (Glover and Kim, 1993; Wilson and Mackay, 1993; Adams, 1995; Bixley *et al.*, 1995; Upstill-Goddard and Wilkins, 1995). SF_6 is an inert, sparingly soluble, and nontoxic gas, resistant to chemical and thermal degradation over a wide range of conditions. In addition, the background concentrations of SF_6 are essentially zero and it is easily analyzed to very low detection limits ($<10^{-17}$ mol) by gas chromatography using an electron capture detector (ECD). SF_6 is also inexpensive and requires no special handling precautions. This unique combination of properties confers many advantages to SF_6 over more conventional tracers such as radioactive ^{133}Xe (Wilson and Mackay, 1993; Upstill-Goddard and Wilkins, 1995).

In high-temperature geothermal fields, however, SF_6 tracer tests have given anomalous results. For example, Glover and Kim (1993) noted that SF_6 acted as a better tracer for liquid water at depth than xenon which is difficult to explain, as the higher volatility of SF_6 would indicate that the reverse should occur. Adams (1995) noted that recovery of SF_6 tracer in liquid water phase tests was much less than in vapor phase tracer tests. He suggested SF_6 was removed from the liquid phase due to its higher density or due to partitioning of SF_6 into steam during boiling in the aquifer.

This study was undertaken because there were no measured Henry's law constants for SF_6 above 50 °C; hence it is difficult to interpret the results of tracer injection tests into high-temperature single-phase and two-phase geothermal aquifers.

Experimental Section

Experimental Procedure. A 100 cm^3 capacity 316 stainless steel (SS) autoclave was filled with approximately 70 cm^3 of degassed distilled water, and the headspace was evacuated and then filled with SF_6 (Montefluos, SF_6 purity >99.97% by mass) to a total pressure less than 0.2 MPa at room temperature. The autoclave was heated in a rocking furnace and the temperature measured with a chromel−alumel thermocouple (±0.2 °C) routinely calibrated against a platinum resistance thermometer (Fluke Y2039). The pressure was measured with a pressure transducer (Lucas Schaevitz P961) with an accuracy of ±12 kPa, which was calibrated with a Budenberg Ranger dead weight tester.

The rocking autoclave was equilibrated at the set temperature overnight and up to three samples were extracted and analyzed the following day (usually 2 h apart). The autoclave was sampled through a 20 mm length of 316 SS capillary tubing (i.d. 0.51 mm) which extended about 10 mm above the bottom of the autoclave. A 200 mm length of 0.25 mm i.d. poly(ether ether ketone) (PEEK) tubing and a 50 mm length of 0.51 mm i.d. PEEK tubing were connected in series to the SS capillary tubing. All the tube sections had the same external diameter of 0.625 mm. A sample was withdrawn into a gastight 50 μL SGE (gas sealing gland) syringe. Syringes and fittings containing Teflon were avoided, as Teflon readily absorbs SF_6 which is then released nonuniformly. The 0.5 mm o.d. syringe needle was passed through a PEEK tube connector and inserted into the 0.51 mm i.d. PEEK tubing. A hollow bolt screwed into the connector compressed a ferrule over the tube and provided a leaktight seal between the needle and inner tube wall. A small clamp pinching the PEEK tube acted as the outlet control valve. This simple arrangement enabled the autoclave to be repeatedly and easily sampled. More importantly, the volume of liquid extracted could be kept to a minimum, less than 100 μL, which included a presample to clear the tube of stagnant fluid. A typical pressure drop during sampling at 4 MPa (≈250 °C) was about 2 kPa, less than the accuracy of the pressure transducer.

Analytical Method. The 50 μL sample was injected into a glass vessel (approximately 1.2 L) containing a magnetically driven Nylon stirrer. The large ratio of the vessel to sample volume and high volatility of SF_6 meant that essentially all the available SF_6 was in the vapor phase. After an initial mixing period of 5 min the vessel was supplied with 100 cm^3 min^{-1} of nitrogen until the SF_6 in the effluent was in the linear range of the ECD and the highest standard (10 nL/L). This usually took about 30 min. The concentration was allowed to decay a further 30 min and the logarithm of the peak areas were extrapolated to zero time to obtain the initial SF_6 concentration. The sample mass was calculated from the difference in syringe mass (Sartorius 2001 MP2 analytical balance weighs to 0.1 mg) before and after injection.

The samples were analyzed using a Varian 3600 gas chromatograph fitted with an ECD with a radioactive ^{63}Ni

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source. The carrier gas was a mixture of 3% volume methane and 97% volume argon at a flow rate of 30 cm^3 min^{-1}. Separation was achieved with a 0.1 m 80−100 mesh Poropak T precolumn at room temperature followed by a 3 m long $^1/_8$ in. diameter column containing 45−60 mesh Molecular Sieve 5A. The precolumn, main column oven, and detector oven were at 21 °C, 50 °C, and 280 °C respectively. The gas phase concentrations measured in this study were well above the detection limit of the machine, which was about 10^{-17} mol using a 0.25 cm^3 sampling loop.

Results and Discussion

Data Reduction. Henry's law constants (k_H) were calculated from the experimental solubility data (Benson and Krause, 1989; Fernández-Prini and Crovetto, 1989; Fernández-Prini *et al.*, 1992) by

$$k_H = \frac{y\phi_2 P}{x} \exp\frac{-V^{\infty}(P - P_s)}{RT} \tag{1}$$

where P_s is the pure water vapor pressure at saturation, P is the total pressure, x and y are the liquid and gas phase SF_6 mole fractions, ϕ_2 is the SF_6 gas phase fugacity coefficient, V^{∞} is the partial molar volume of SF_6 at infinite dilution, R is the universal gas constant, and T is the absolute temperature. The activity coefficients of dissolved SF_6 were assumed to be unity, a reasonable assumption given the low solubility of this gas. V^{∞} was assumed to be close to the molar volume of SF_6 at its normal boiling temperature which was estimated to be 73 cm^3 mol^{-1} using the Tyn and Calus method (Reid *et al.*, 1988). The total pressure was close to the pure water vapor pressure so that the second term of eq 1 is near unity across the whole temperature range and is not sensitive to large variations (±30%) in V^{∞}.

The vapor phase mole fraction (y) of SF_6 in eq 1 was calculated by

$$1 - y = \frac{(1 - x)\phi_s P_s}{\phi_1 P} \exp\frac{V_s(P - P_s)}{RT} \tag{2}$$

where ϕ_s is the pure water fugacity coefficient at saturation, ϕ_1 is the gas phase fugacity coefficient of water, and V_s is the molar volume of pure liquid water at saturation.

The fugacity coefficients of the components as well as that of pure water were calculated using the Peng−Robinson cubic equation of state (Reid *et al.*, 1988, Fernández-Prini and Crovetto, 1989; Fernández-Prini *et al.*, 1992). The mixing interaction parameter required in the equation of state was assumed to be 0.5, a value found to apply for a large number of nonpolar gas−water systems (Fernández-Prini and Crovetto, 1989).

The dimensionless gas distribution coefficient, B, used to model partitioning of tracer in two-phase geothermal aquifers, is defined as the concentration of gas in vapor divided by the concentration of gas in liquid.

$$B = \frac{y(1 - x)}{(1 - y)x} \tag{3}$$

The measured SF_6 solubilities and pressures are presented in Table 1. Henry's law constants and the distribution coefficients were calculated for each experimentally determined solubility.

Table 1. Experimental Solubility Data for Sulfur Hexafluoride in Water

t/°C	P/MPa	P_s/MPa	$10^6 b$/ mol kg^{-1}	$10^6 x$	y	ln(k_H/ MPa)	ln B
74.1	0.164	0.037	172	3.09	0.774	10.61	13.91
74.3	0.165	0.037	178	3.21	0.775	10.58	13.89
74.3	0.164	0.037	180	3.24	0.774	10.56	13.87
74.4	0.162	0.038	174	3.13	0.765	10.57	13.85
99.2	0.226	0.099	153	2.75	0.560	10.72	13.04
99.2	0.224	0.099	157	2.84	0.556	10.68	13.00
99.2	0.225	0.099	153	2.76	0.558	10.71	13.03
124.1	0.350	0.226	167	3.00	0.350	10.61	12.10
124.3	0.350	0.227	159	2.87	0.347	10.64	12.13
124.4	0.558	0.228	421	7.59	0.587	10.65	12.14
124.5	0.349	0.229	166	2.99	0.340	10.58	12.06
124.5	0.555	0.229	402	7.25	0.582	10.68	12.17
124.5	0.556	0.229	450	8.11	0.583	10.57	12.06
124.7	0.559	0.230	405	7.30	0.584	10.68	12.17
124.8	0.560	0.231	410	7.38	0.583	10.67	12.15
148.5	0.553	0.457	159	2.87	0.169	10.39	11.17
148.6	0.554	0.459	145	2.61	0.167	10.48	11.25
148.8	0.556	0.461	155	2.79	0.166	10.41	11.18
152.2	0.626	0.505	192	3.47	0.188	10.43	11.11
152.3	0.626	0.506	191	3.43	0.186	10.43	11.11
152.5	0.626	0.509	189	3.40	0.182	10.42	11.09
162.0	0.970	0.650	594	10.70	0.320	10.26	10.69
162.2	0.974	0.653	555	10.00	0.320	10.33	10.76
162.5	0.978	0.658	524	9.45	0.317	10.39	10.80
178.5	1.047	0.968	173	3.12	0.072	10.10	10.12
178.7	1.050	0.972	167	3.01	0.070	10.12	10.13
178.8	1.053	0.975	176	3.17	0.070	10.07	10.08
206.2	1.858	1.764	274	4.94	0.046	9.80	9.19
206.3	1.860	1.768	255	4.59	0.045	9.85	9.24
206.3	1.857	1.768	249	4.48	0.044	9.84	9.23
231.8	2.951	2.888	220	3.97	0.019	9.60	8.47
232.2	2.975	2.909	214	3.86	0.019	9.68	8.54
232.4	2.983	2.920	236	4.25	0.018	9.53	8.39

Table 2. Literature Solubility Data for Sulfur Hexafluoride in Water

t/°C	P/MPa	P_s/MPa	$10^6 x$	y	ln(k_H/MPa)	ln B
Cosgrove and Walkley (1981)						
25	0.104 49	0.003 17	4.43	0.970	10.02	15.79
30	0.105 57	0.004 25	3.87	0.960	10.16	15.63
35	0.106 95	0.005 63	3.49	0.947	10.26	15.46
40	0.108 71	0.007 39	3.23	0.932	10.34	15.26
Ashton *et al.* (1968)						
25	0.104 49	0.003 17	4.39	0.970	10.03	15.80
27.5	0.105 00	0.003 67	4.09	0.965	10.10	15.72
30	0.105 57	0.004 25	3.86	0.960	10.16	15.64
35	0.106 95	0.005 63	3.47	0.947	10.27	15.46
40	0.108 71	0.007 39	3.23	0.932	10.34	15.26
45	0.110 92	0.009 60	3.03	0.913	10.40	15.06
50	0.113 68	0.012 35	2.86	0.891	10.46	14.87

The aqueous solubility of SF_6 under 101.325 kPa of gas has been measured between 2.5 °C and 50 °C by Ashton *et al.* (1968) and between 5 °C and 40 °C by Cosgrove and Walkley (1981). Henry's law constants and distribution coefficients derived from their data using the Peng−Robinson equation of state are listed in Table 2. A least squares fit of the data in Tables 1 and 2 showed that the empirical equations that best describe the temperature dependence of ln k_H and ln B within the experimental errors are expressed by

$$\ln(k_H/MPa) = \ln(P_s/MPa) - \frac{14.8637}{T^*} + \frac{2.1337(1 - T^*)^{0.355}}{T^*} + 18.82(T^*)^{-0.41} \exp(1 - T^*) \tag{4}$$

$$\ln B = 26.4987 - 0.03609(T/\mathrm{K}) \tag{5}$$

where T^* is the reduced temperature T/T_c and T_c = 647.096 K. The smoothed results are listed in Table 3. The form of eq 4 has been shown by Harvey (1996) to successfully predict the high-temperature Henry's constants for a number of solutes as the solvent's critical temperature is

Table 3. Smoothed Henry's Law Constants (k_H) and Vapor–Liquid Distribution Coefficients (B)

t/°C	ln(P_s/MPa)	ln(k_H/MPa)	ln B
25	−5.754	10.04	15.74
50	−4.394	10.46	14.84
75	−3.255	10.65	13.93
100	−2.289	10.68	13.03
125	−1.460	10.60	12.13
150	−0.742	10.43	11.23
175	−0.114	10.21	10.32
200	0.441	9.94	9.42
225	0.936	9.65	8.52
230	1.029	9.59	8.34
250[a]	1.380	9.33	7.63
300[a]	2.150	8.66	5.81

[a] Extrapolated values.

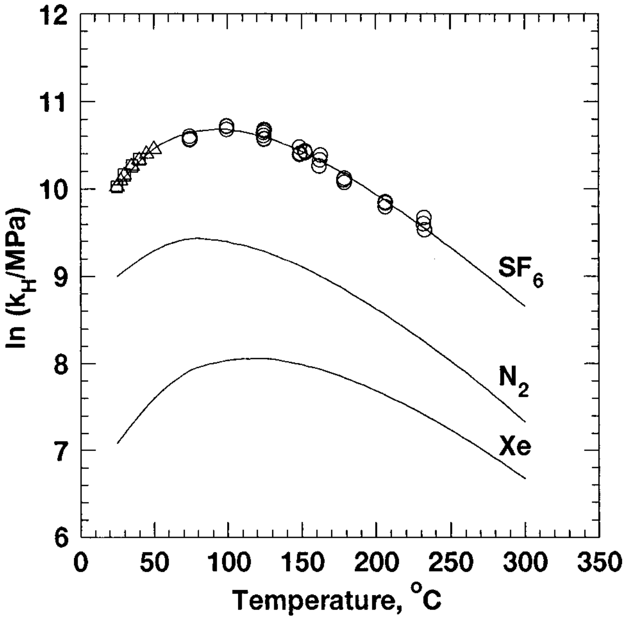

Figure 1. Henry's law constants: (○) this work; (△) Ashton et al. (1968); (□) Cosgrove and Walkley (1981); Xe and N_2 correlations from Harvey (1996).

approached. The solvent vapor pressure P_s for water was calculated with the equation of Wagner and Pruss (1993), using a value of 647.096 K for the critical temperature.

The experimental and smoothed Henry's constant results are presented in Figure 1. For comparison, data for xenon, commonly used as a radioactive tracer, and nitrogen, one of the less soluble geothermal gases (Harvey, 1996), are also included in Figure 1. At 100 °C, SF_6 is approximately 4 and 14 times less soluble than nitrogen and xenon respectively, and at 200 °C, 3 and 7 times less soluble, respectively.

The linear relationship between ln B and temperature is shown in Figure 2. Adams (1995) derived an equation for the SF_6 distribution coefficients at elevated temperatures from low-temperature Henry's constant data. There is good agreement between the present results and his extrapolated values (Figure 2).

Errors. Direct sampling of liquid from an autoclave is usually difficult because of the problems of losing gas into the vapor phase during sampling. The small sample volumes extracted seem to have avoided this problem, leading to acceptable reproducibility in the measured solubilities (Table 1). The analysis error estimated from repeat measurements of samples and standards, within the linear range of the ECD detector, was less than 5%. However, the standard errors of the concentrations at zero time, calculated by extrapolating back to the commencement of dilution, were higher, typically 10%. The repeatability within the estimated errors also showed that loss of SF_6 through the needle vent bore (~0.2 mm i.d.) was apparently not a problem. Wilson and Mackay (1993) suggested loss through the vent would be minimized due to the high density of the gas.

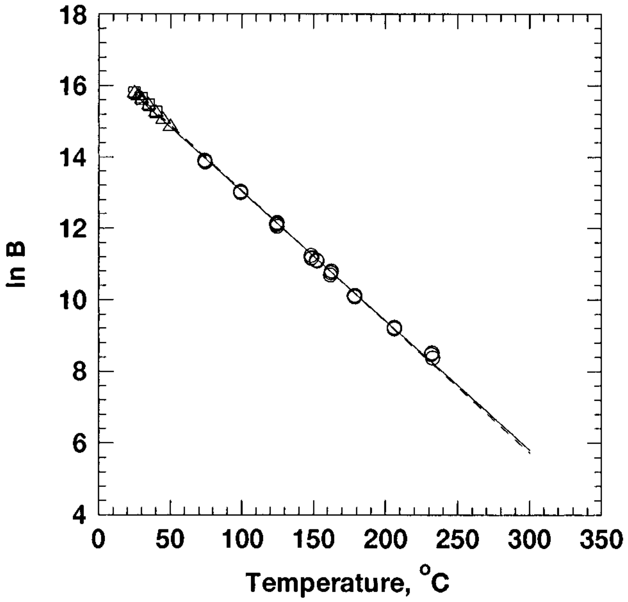

Figure 2. Distribution coefficients: (○) this work; (△) Ashton et al. (1968); (□) Cosgrove and Walkley (1981); (- - -) Adams (1995).

The accuracy of Henry's law constant also depends on the precision with which the partial pressure of gas can be measured. At temperatures above 225 °C, the uncertainty increases because of the increased temperature dependence of the water vapor pressure. At 225 °C the uncertainty in the temperature measurement gives rise to uncertainty in water vapor pressure of ±10 kPa, similar to the accuracy of the total pressure measurement.

Given the estimated uncertainties in the gas analysis and pressure measurements, the accuracy of the Henry's law constants determined in this study are realistically about 10% at 75 °C, increasing to 20−30% at temperatures above 200 °C. The reasonable fit of the data suggests the precision of the measurements is much better than the accuracy would indicate. In the literature there are large uncertainties in Henry's law constant data for sparingly soluble gases at high temperatures, which reflects the difficulty of performing such experiments. The precision of solubility data close to room temperature is 1−2 orders of magnitude higher than data above the normal boiling point of the solvent (Fernández-Prini and Crovetto, 1989).

The Peng−Robinson equation of state is known to adequately describe H_2O−nonpolar gas equilibria at pressures near saturation (Fernández-Prini and Crovetto, 1989; Reid *et al.*, 1988). At the highest temperature (230 °C) the calculated vapor phase mole fraction of SF_6 was 13% lower than that calculated by assuming Dalton's law. The correction for nonideal behavior was less than the experimental uncertainties across the whole temperature range.

Behaviour at High Temperatures. Increasing the mass of SF_6 in the SS vessel to increase the partial pressure of SF_6 in order to compensate for the decrease in precision of the pressure measurement above 200 °C failed because of an unusually abrupt drop in gas partial pressure. Increasing the mass also decreased the temperature at which there was an obvious departure from Henry's law. The readings were stable and reproducible when ap-

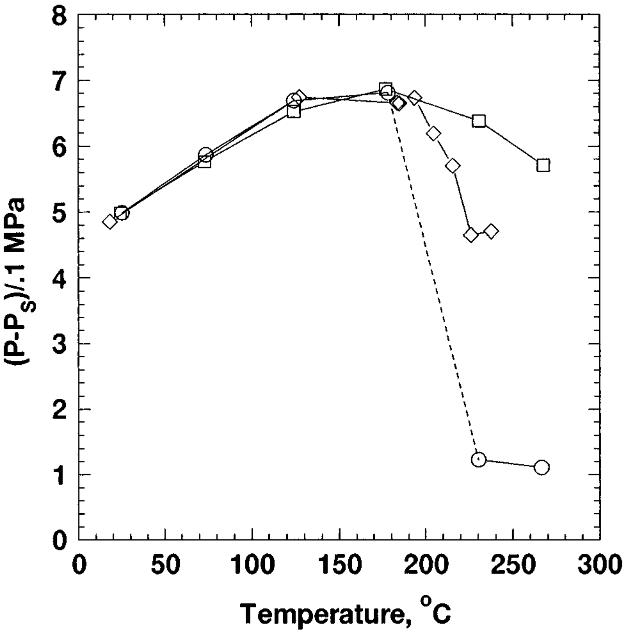

Figure 3. Temperature dependence of partial pressure of SF_6 and N_2. Run 1: 46 cm^3 headspace at 267 °C (○, SF_6; □, N_2). Run 2: 38 cm^3 headspace at 240 °C (◇, SF_6).

proached from a lower or higher temperature. This suggested that the deviation was due to changes in the vessel rather than an error in the analysis or loss of gas during sample collection.

The decrease in partial pressure was initially thought to be due to a leak in the autoclave plumbing but the pressures were reversible on decreasing the temperature. The effect is illustrated in Figure 3 which shows the change in $P(SF_6)$ on increasing the temperature to 267 °C. The autoclave, which was not sampled in this run, was filled with 60 cm^3 of water and 0.5 MPa of gas at room temperature. The mass of gas in the vessel was constant while the headspace volume decreased with increased temperature due to the expansion of water in the vessel. The headspace volume at 267 °C was approximately 46 cm^3, which included the volume of the tube fittings at the top of the vessel. At temperatures between 200 °C and 210 °C there was a sharp drop in partial pressure (Figure 3, run 1). Eventually, the partial pressure stopped decreasing so that between 230 °C and 267 °C the change was less than the uncertainties in the pressure measurement. With a smaller head space in the vessel (Figure 3, run 2) the pressure appeared to stabilize at a higher final partial pressure of gas. The partial pressure curve for nitrogen matched the trend for SF_6 up to 200 °C but thereafter showed a much more gradual decline without any abrupt change in pressure. The change in the gas partial pressures for both gases should have followed a similar trend except that the nitrogen partial pressure was expected to decline at a faster rate due to the higher solubility of this gas.

Whether the drop in gas partial pressure and Henry's law deviation were due to an onset of significant interactions between SF_6 and H_2O or an unrecognized experimental artifact could not be established with the present experimental method. The observed decrease in SF_6 partial pressure as well as a decrease in the solubility suggests that a dense immiscible SF_6 or $SF_6 + H_2O$ binary phase may be forming and removing gas from the vapor and liquid water. This result also explains the anomalous behavior of SF_6 as reported in recent tracer tests. The critical temperature of pure SF_6 is 45.6 °C (Cole and de Reuck, 1990), well below the temperatures used in these experiments, so condensation of the liquid gas cannot account for the observed effect.

Conclusions

The solubility of SF_6 has been measured between 75 °C and 230 °C and empirical equations, describing the temperature dependence of Henry's law constant and the vapor/liquid distribution coefficients have been derived between 25 °C and 230 °C. The form of the Henry's law equation is suitable for extrapolating values to temperatures approaching the critical point of water.

Above 210 °C deviation from Henry's law occurs and there was an unexpected and abrupt drop in measured SF_6 partial pressures with increasing temperature. The reason for these deviations could not be ascertained in the present series of experiments. It is possible the deviation is an experimental artifact. The formation of a dense phase can, however, explain the anomalous behavior of SF_6 reported in injection trials of this gas into high-temperature geothermal fields. The vapor/liquid equilibrium of SF_6 + water mixtures needs further investigation at temperatures above 200 °C.

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