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Measurement of Thermodynamic Properties for the System Sulfur Hexafluoride + Water

B. Strotmann, K. Fischer, and J. Gmehling*

Technische Chemie, Universität Oldenburg, Fachbereich 9, Postfach 2503, 26111 Oldenburg, Germany

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Isothermal *P*, *x* data at 293 K and excess enthalpies (H^E) at 323 K were measured for the binary system sulfur hexafluoride + water using a static apparatus and an isothermal flow calorimeter. This system exhibits heteroazeotropic three phase behavior at 293 K. From the *P*, *x* data in the diluted region of sulfur hexafluoride the Henry constant was derived. A comparison with solubility data available from literature shows good agreement.

Introduction

Several experimental gas solubility data for the system sulfur hexafluoride + water are available from literature. The published data of Friedmann (1954), Morrison and Johnstone (1955), Ashton et al. (1968), Power and Stegall (1970), Longo et al. (1970), Cosgrove and Walkley (1981), Park et al. (1982), and Mroczek (1997) are in good agreement with each other and cover the temperature range between 273 and 505 K. In this range, the Henry constants of sulfur hexafluoride increase from 8.5 GPa at 273 K, reach a maximum of 45 GPa at ~373 K, and then decrease to 11 GPa at 505 K. This indicates an extremely low solubility, even smaller than helium, for which the maximum value of the Henry constant as a function of temperature is lower than 20 GPa (~313 K), or methane (7 GPa, ~363 K), hydrogen (8 GPa, ~343 K), nitrogen (15 GPa, ~343 K), and carbon monoxide (6 GPa, ~403 K), although the critical temperature of sulfur hexafluoride is 318.75 K and all the other components mentioned show critical temperatures lower than 200 K.

The exception of sulfur hexafluoride in the series of volatile substances becomes apparent in Figure 1, where the maximum of the Henry coefficients of the different gases in water as a function of temperature are plotted against the critical temperature of the gases. The temperature, where this maximum is reached, as a function of the critical temperature of the gas is shown in Figure 2. In both plots, the dependence of the critical temperatures appears to be quite significant, and the solubility behavior of sulfur hexafluoride is unusual.

The binary system was studied as part of an ongoing investigation sponsored by Project 805c/95, Design Institute for Physical Property Data of the American Institute of Chemical Engineers.

The large Henry constants in combination with the vapor pressure of sulfur hexafluoride (critical pressure, 3.76 MPa) allow one to conclude that for the subcritical temperature range the liquid will split into two phases, whereby the mutual solubility is very small. For a further understanding of the thermodynamic behavior of this unusual binary system, additional experimental information is desired. In this work, the boiling point curve (*P*−*x* data) at ca. 293 K and the excess molar enthalpy (H^E data) at 323 K of the system sulfur hexafluoride + water were measured using a static apparatus and an isothermal flow calorimeter.

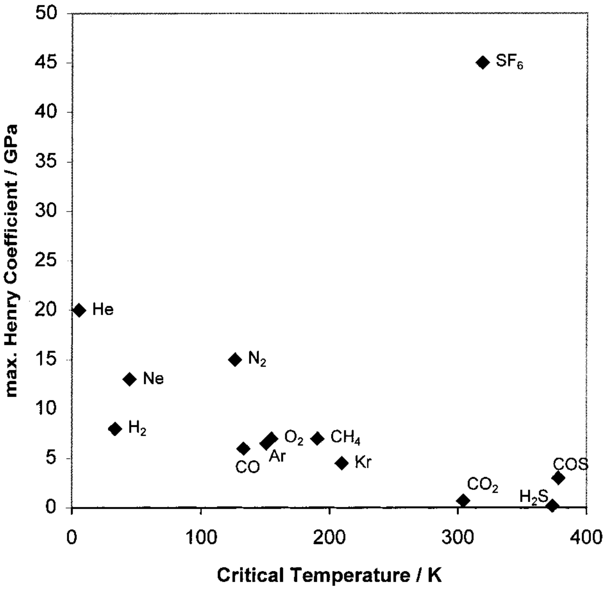

Figure 1. Plot of the maximum Henry coefficient for different volatile compounds in water as a function of the critical temperature of the gases (data source: Dortmund Data Bank (DDB)).

Experimental Section

Water was distilled twice and carefully degassed by distillation, as described previously by Fischer and Gmehling (1994). Sulfur hexafluoride was supplied as a liquified gas by Messer-Griesheim with a purity better than 99.9%. Because the homogeneous liquid was expected to be stable only for extremely diluted solutions, special attention was paid to remove the last traces of water from the sulfur hexafluoride. The liquid sulfur hexafluoride was stored under pressure for more than 1 day over phosphorous pentoxide in a steel container from where it was directly distilled into the injection pumps.

Vapor−Liquid Equilibrium. The static apparatus used was previously described in detail by Fischer and Gmehling (1994). A stirred equilibrium cell is placed in a constant-temperature bath. The components are charged using precise piston injectors. The system pressure at a given temperature and composition was measured using precise balance gauges.

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* Corresponding author. Telephone: ++49 441 798 3831. Fax: ++49 441 798 3330. E-mail: gmehling@fb9tc.uni-oldenburg.de.

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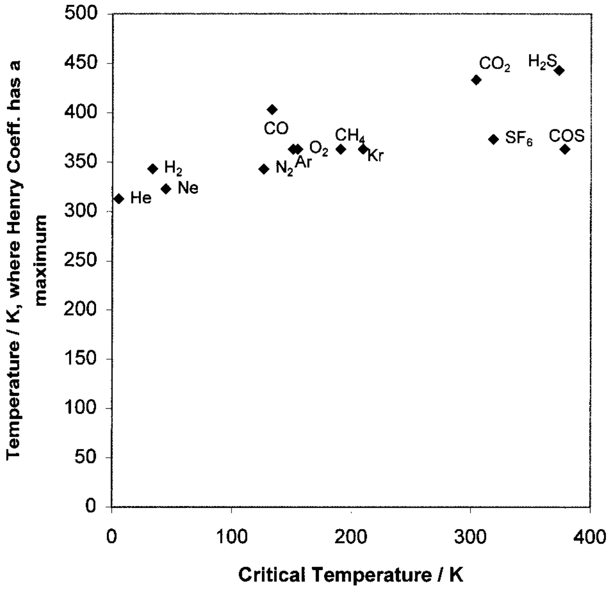

Figure 2. Plot of the temperature, where the Henry coefficient of different volatile compounds in water reach a maximum value, as a function of the critical temperature of the gases (data source: DDB).

Procedure. (a) Pure liquid sulfur hexafluoride (ca. 105 cm^3) was charged into the evacuated equilibrium cell (total volume, ca. 195 cm^3) using a displacement pump. The volume of sulfur hexafluoride in the piston injector was determined accurately before and after the injection at 293 K and 4 MPa. Then the vapor pressure of sulfur hexafluoride was measured at a given temperature (292.85 K) of the equilibrium cell. From a second displacement pump a small amount of water (<0.01 cm^3) was injected. After ca. 30 min, equilibrium was reached and the system pressure was measured. The injection of water was repeated, whereby an increasing system pressure was observed with the admixture of water. After ca. five injections, the system pressure remained constant until ca. 50 cm^3 of water had been charged into the equilibrium cell. From the constant pressure it can be concluded, that the system exhibits a miscibility gap. Since the three phase pressure was above the vapor pressure of pure sulfur hexafluoride, it can be concluded that the system shows heteroazeotropic behavior.

After cleaning the equilibrium cell, the whole procedure was restarted, starting with the injection of pure water. Then a very small amount of sulfur hexafluoride was added. Despite the small amount of sulfur hexafluoride added the three phase pressure was observed, because of the extremely small solubility. To measure also data in the homogeneous region of extremely diluted sulfur hexafluoride, a different procedure was applied.

(b) From the piston injector, a small amount of pure sulfur hexafluoride was evaporated into the equilibrium chamber. Then a valve was opened to remove sulfur hexafluoride by vacuum until only a small partial pressure (ca. 2.7 kPa) was reached. Water was added stepwise and the system pressure was measured after every injection as described above until the pressure exceeded the three phase pressure, and the vapor phase thus completely disappeared. It is worth mentioning, that with decreasing volume of the vapor phase the time to reach equilibrium increased from 30 min to more than 24 h. The same procedure was repeated, whereby the initial partial pressure of sulfur hexafluoride was set to 12.0 kPa.

Derivation of P−x Data. (a) The molar amount of liquid substances charged into the equilibrium cell can be derived from the volume difference of the liquids in the displacement pumps before and after injection. The molar volumes of the liquids were calculated for the temperature of the thermostated piston injectors using interpolated experimental liquid density data. These volumes were corrected using the compressibility of the components to the reference pressure (4 MPa). The compressibility was roughly determined from the *PV* behavior of the liquids in the displacement pumps.

From the molar amounts of substances injected, the feed composition can be calculated. In an article by Fischer and Gmehling (1994), an iterative procedure was described to determine the liquid composition from the feed composition. The difference between the feed and the liquid composition usually is very small, because the amounts of substances in the vapor phase are almost negligible compared to those in the liquid phase. For the description of the vapor phase, the second virial coefficients were taken into account ($B_{SF_6} = -290.11$ cm^3 mol^{-1} at 292.85 K, recommended by Daubert and Danner (1985)).

(b) The molar amount of gaseous sulfur hexafluoride could be derived from the *PVT* behavior (interpolated experimental second virial coefficient). From the molar amounts of substances injected, the feed composition can be calculated. But due to the extremely small solubility of sulfur hexafluoride in water almost the total amount of the charged sulfur hexafluoride is in the vapor phase. Therefore only for those points where the vapor phase almost disappeared by injection of water, the following calculation was performed. For both runs (initial pressure, 2.7 or 12.0 kPa) the last two points below the three phase pressure were chosen, because in those cases the vapor volume was small (0.1−3 cm^3). For these points, the portion of sulfur hexafluoride in the vapor phase was between 12 and 74%.

From the raw experimental data, the exact volume of the equilibrium cell was determined. It was identical with the volume of injected water for the system pressure of 4 MPa, because the very small amount of sulfur hexafluoride does not significantly change the molar volume of water.

$$V^{L} = V^{L}_{H_2O}$$

The total molar amount of sulfur hexafluoride $n^{T}_{SF_6}$ was determined using the measured pressure P, temperature T, and total volume of the equilibrium cell V^{T} and the second virial coefficient B_{SF_6} at a given temperature. The partial pressure of sulfur hexafluoride can be calculated from the difference between the total pressure and the vapor pressure of pure water $P^{s}_{H_2O}$

$$P_{SF_6} = P - P_{H_2O}$$

because the activity of the almost pure water is equal to 1 and the partial pressure of water P_{H_2O} is equal to the vapor pressure of water:

$$P_{SF_6} = P - P^{s}_{H_2O}$$

To obtain the volume of the vapor phase, the difference between the total volume of the equilibrium cell and the liquid volume is calculated:

$$V^{V} = V^{T} - V^{L}$$

This equation has to be solved iteratively, whereby the starting value for the liquid volume was the liquid volume of all water injected. For the calculation of the volume of

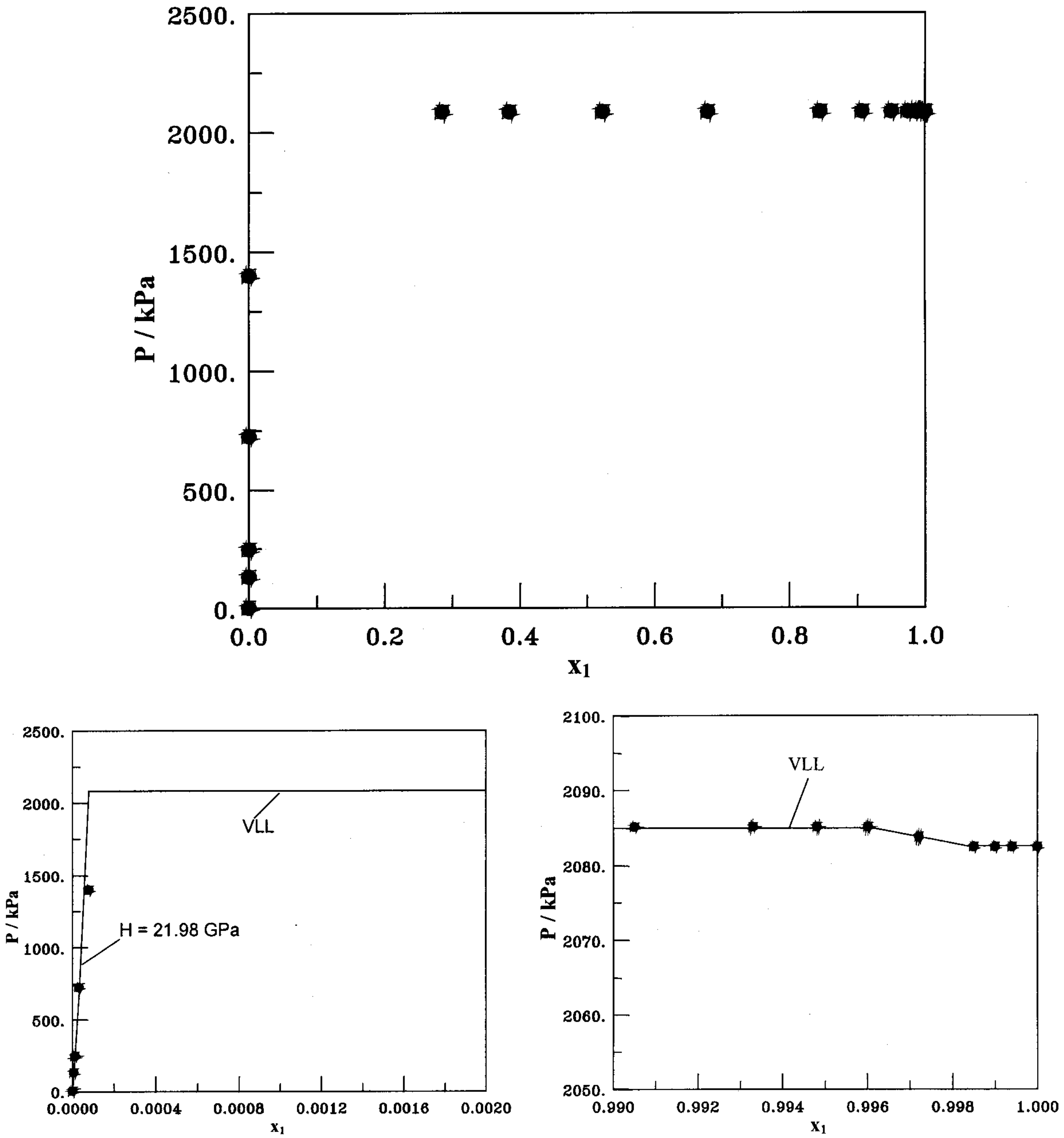

Figure 3. Experimental $P-x$ data for the system sulfur hexafluoride (1) + water (2) at 292.85 K.

liquid water, also the compressibility of water was taken into account. From the vapor volume and the partial pressure (=vapor pressure as explained above) of water, the molar amount of water in the vapor phase was calculated and the volume of the remaining liquid water recalculated. Convergence was reached after a few cycles and the obtained vapor volume, temperature, and partial pressure of sulfur hexafluoride was used to calculate the molar amount of sulfur hexafluoride in the vapor phase using the second virial coefficient at the given temperature. The difference between the total molar amount and the amount in the vapor phase for both components is given by

$$n_i^{\mathrm{L}} = n_i^{\mathrm{T}} - n_i^{\mathrm{V}}$$

from which the mole fraction of SF_6 in the liquid phase can be calculated.

Heats of Mixing. A commercial isothermal computer driven flow calorimeter (Hart Scientific, Model 7501) and the procedure used in the present study are the same as those outlined by Gmehling (1993). In this type of calorimeter, the heat effects, which occur during mixing, are compensated for with the help of a pulsed electric heater. A Peltier cooler allows us to control the frequency of the pulsed heater and to set the baseline, so that also exothermal heat of mixing effects can be determined. Two runs using different total flow rates of 40/80 $cm^3\ h^{-1}$ were performed. Pure component densities and the molar masses provide the total mole flow. Unfortunately it was not possible to measure precise data in the homogeneous regions, because of the small flow rates.

Results

The experimental $P-x$ data are listed in Table 1 and shown in Figure 3. The data show a large miscibility gap for the system sulfur hexafluoride + water at 293 K. The data within the miscibility gap are marked in Table 1. Some data points were measured in the homogeneous

Table 1. Experimental $P-x$ Data for the System Sulfur Hexafluoride (1) + Water (2) at 292.85 K

x_1	P/kPa	x_1	P/kPa	x_1	P/kPa
0	2.29	0.6783	2085.0[a]	0.9948[a]	2085.0
5.11×10^{-6}	132.63	0.8446	2085.1[a]	0.9960[a]	2084.8
1.14×10^{-5}	247.74	0.9067	2085.1[a]	0.9972[a]	2083.6
3.14×10^{-5}	725.52	0.9499	2085.0[a]	0.9985[a]	2082.9
7.87×10^{-5}	1400.2	0.9742	2084.9[a]	0.9990	2082.8
0.2846	2085.3[a]	0.9844	2085.1[a]	0.9994	2083.0
0.3841	2085.4[a]	0.9905	2084.8[a]	1	2082.6
0.5223	2085.2[a]	0.9933	2084.9[a]		

[a] Two liquid phases.

Table 2. Derived Henry Constants of Sulfur Hexafluoride (1) in Water (2) at ca. 293 K

H_{12}/GPa	ref	H_{12}/GPa	ref
21.98	this work	20.1	Ashton et al. (1968)
20.3	Longo et al. (1970)	19.7	Cosgrove and Walkley (1981)

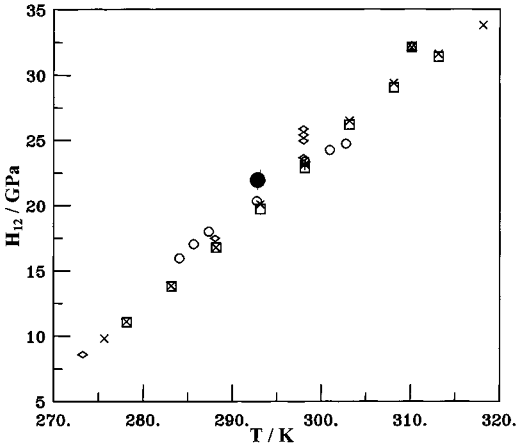

Figure 4. Experimental Henry constants of sulfur hexafluoride in water as a function of temperature (zoomed temperature range: ●, this work; other symbols, literature data).

regions. From the points in the diluted region of sulfur hexafluoride the Henry constant was determined by linear regression of P_i vs x_i data. The Henry constant is given in Table 2 and compared with literature data at approximately 293 K. Agreement of the Henry constants is obtained within 10%. The experimental Henry constants as given in the literature are plotted vs temperature in Figures 4 and 5. It can be seen that the Henry coefficients show a maximum. The P, x data in the homogeneous region of diluted water show that the system pressure increases from the vapor pressure of pure sulfur hexafluoride (2082.6 kPa) up to the three phase pressure (2085 kPa). The difference between these pressures (2.4 kPa) is almost identical with the vapor pressure of pure water (2.29 kPa). Therefore it can be concluded that the system sulfur hexafluoride + water exhibits heteroazeotropic behavior. The azeotropic composition can be estimated from the ratio of the vapor pressures.

$$y_1 = \frac{P_1^s}{P_1^s + P_2^s}$$

The temperature, pressure, and composition of the heteroazeotropic point are given in Table 3.

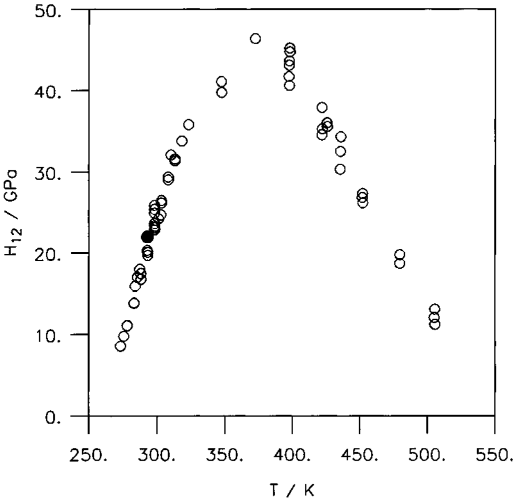

Figure 5. Experimental Henry constants of sulfur hexafluoride in water as function of temperature (entire temperature range: ●, this work; ○, literature data).

Table 3. Heteroazeotropic Point Derived from Experimental $P-x$ Data

T/K	322.85
P/MPa	2.085
y_1	0.9988

Table 4. Experimental Heat Effects for the System Sulfur Hexafluoride (1) + Water (2) at 323.15 K and 9.5 MPa

x_1	H^E/(J mol^{-1})	x_1	H^E/(J mol^{-1})	x_1	H^E/(J mol^{-1})
0.0106	4.47	0.0990	8.62[a]	0.3798	1.26[a]
0.0165	1.00	0.1198	8.10[a]	0.4495	−2.30[a]
0.0222	9.77	0.1431	6.98[a]	0.5363	−5.01[a]
0.0224	0.88	0.1710	4.79[a]	0.6475	−6.92[a]
0.0348	8.77	0.1997	4.92[a]	0.7950	−13.22[a]
0.0485	8.60	0.2344	5.25[a]	0.9422	−15.94[a]
0.0637	9.24[a]	0.2749	3.92[a]	0.9704	−16.76[a]
0.0804	9.24[a]	0.3226	3.18[a]	0.9850	−17.59[a]

[a] Two phases.

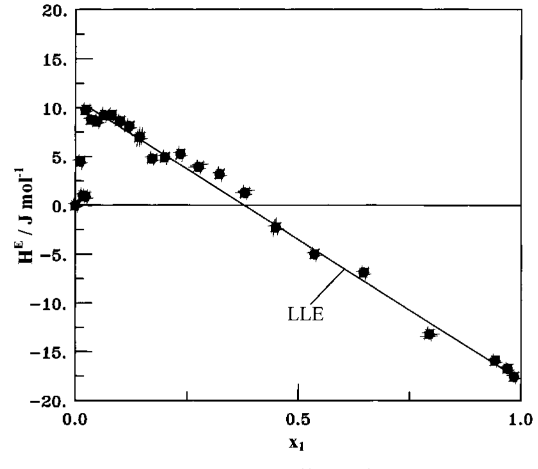

Figure 6. Experimental heat effects for the system sulfur hexafluoride (1) + water (2) at 323.15 K and 9.5 MPa.

The measured heat of mixing data are given in Table 4 and shown in Figure 6. It can be seen, that the two phase region is indicated by a straight line. The heat effects at 323 K, which is slightly above the critical temperature of sulfur hexafluoride, show very small values caused by the small mutual solubilities. On the water rich side, the system shows endothermic heat effects, and on the sulfur hexafluoride rich side, exothermic heat effects are obtained. Due to the very small heat effects and also because of the problem of achieving a small constant flow of sulfur hexafluoride, a scattering of the H^E data was observed.

Discussion

$P-x$ data at 293 K and H^E data at 323 K were measured for the system sulfur hexafluoride + water. The measured data show good agreement with the experimental gas solubility data available from literature. It was confirmed by eight previous publications that the solubility of sulfur hexafluoride in water is very low. It was experimentally proved by the existence of a constant three phase pressure that liquid mixtures of sulfur hexafluoride and water form two liquid phases. Since the three phase pressure is above the vapor pressure of sulfur hexafluoride, it can be concluded that the system shows a heteroazeotropic point. Very small enthalpy effects, endothermal on the water rich and exothermal on the sulfur hexafluoride rich sides, were found. The H^E data also indicate a large two phase region.

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Literature Cited

Ashton, J. T.; Dawe, R. A.; Miller, K. W.; Smith, E. B.; Dickings, B. J. The Solubility of Certain Gaseous Fluorine Compounds in Water. *J. Chem. Soc.* **1968**, 1793−1796.

Cosgrove, B. A.; Walkley, J. Solubilities of Gases in H_2O and D_2O. *J. Chromatogr.* **1981**, *216*, 161−167.

Daubert, T. E.; Danner, R. P. *Data Compilation, Tables of Properties of Pure Compounds*; AIChE: New York, 1985.

Fischer, K.; Gmehling, J. $P-x$ and γ^∞ Data for the Different Binary Butanol−Water Systems at 50 °C. *J. Chem. Eng. Data* **1994**, *39*, 309−315.

Friedmann, H. L. The Solubilities of Sulfur Hexafluoride in Water and of the Rare Gases, Sulfur Haxafluoride, and Osmium Tetroxide in Nitromethane. *J. Am. Chem. Soc.* **1954**, *76*, 3294−3297.

Gmehling, J. Excess Enthalpies for 1,1,1-Trichloroethane with Alkanes, Ketones, and Esters. *J. Chem. Eng. Data* **1993**, *38*, 143−146.

Longo, L. D.; Delivoria-Papadopoulos, M.; Power, G. G.; Hill, E. P.; Forster, R. E. Diffusion Equilibration of Inert Gases between Maternal and Fetal Placental Capillaries. *Am. J. Physiol.* **1970,** *219* (3), 561−569.

Morrison, T. J.; Johnstone, N. B. B. The Salting-out of Non-Electrolytes. Part III. Inert Gases and Sulphur Hexafluoride. *J. Chem. Soc.* **1955**, 3655−3659.

Mroczek, E. K. Henry's Law Constants and Distribution Coefficients of Sulfur Hexafluoride in Water from 25 °C to 230 °C. *J. Chem. Eng. Data* **1997**, *42*, 116−119.

Park, T.; Rettich, T. R.; Battino, R.; Peterson, D.; Wilhelm, E. Solubility of Gases in Liquids. 14. Bunsen Coefficients for Several Fluorine-Containing Gases (Freons) Dissolved in Water at 298.15 K. *J. Chem. Eng. Data* **1982**, *27*, 324−326.

Power, G. G.; Stegall H. Solubility of Gases in Human Red Blood Cell Ghosts. *J. Appl. Physiol.* **1970**, *29*, 145−149.

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