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Henry's Law Constant Measurements of $CHClF_2$, CH_2F_2, C_2HF_5, CH_2FCF_3, and CH_3CHF_2 in Ethanol and Methanol with Headspace Gas Chromatography

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Henry's law constants of hydrofluorocarbons in alcohols were measured with headspace gas chromatography. Isothermal vapor−liquid equilibria for 10 fluorocarbon + alcohol systems ranging from 303 to 323 K were also measured. The experimental data of chlorodifluoromethane ($CHClF_2$, HCFC22), difluoromethane (CH_2F_2, HFC32), pentafluoroethane (C_2HF_5, HFC125), 1,1,1,2-tetrafluoroethane (CH_2FCF_3, HFC134a), and 1,1-difluoroethane (CH_3CHF_2, HFC152a) in either methanol or ethanol were correlated as a function of temperature with the Valentiner equation.

Introduction

Chlorofluorocarcbons (CFCs) and hydrochlorofluorocarbons (HCFCs) containing chlorine have been widely used since 1926 because of their low toxicity and chemical stability. However, their production will be reduced or eliminated in the near feature because of their ozone depletion potential. One of the authors proposed a photodecomposition process, which removes chlorine atoms from chlorinated compounds such as CFCs or HCFCs dissolved in an alcohol.[1−3] To design a photochemical reactor according to the above new process, solubilities of CFC or HCFC in alcohol were required. Henry's law constants for 21 fluorocarbon + alcohol systems ranging from 283 to 313 K at atmospheric pressure were determined in our previous work.[4] Measurement of vapor−liquid equilibrium consumes much time and effort. In this work, we applied headspace analysis to obtain Henry's law constant data from isothermal vapor−liquid equilibrium measurements for fluorocarbon + alcohol systems at temperatures ranging from 303 to 323 K.

Experimental Section

Materials. Both ethanol and methanol with purities of 99.5% were obtained from Kanto Chemical Industries (Tokyo). HFC134a, HFC125, HFC32, HFC152a, and HCFC22 with purities of 99.9% were obtained from Toei Chemical Industries (Tokyo). All chemicals were used as supplied without further purification.

Apparatus and Procedure. A Perkin-Elmer headspace autosampler gas chromatography (HS-40) was used. As shown in Figure 1, this system consisted of autosampler gas chromatography with a thermal conductivity detector (TCD) and an integrator. Glass vials with 22 mL capacity were used as equilibrium cells. The autosampler was held in a constant-temperature bath that could obtain 13 vials. The temperature was measured with platinum-resistant temperature sensors to within an estimated uncertainty of ±0.1 K.

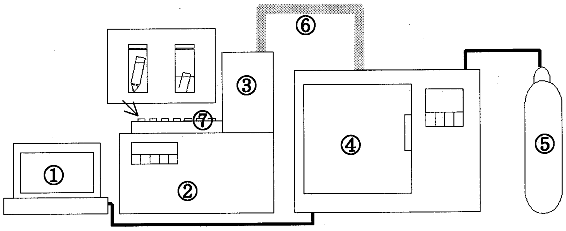

Figure 1. Experimental apparatus: 1, integrator; 2, autosampler; 3, thermostat unit and sampling syringe; 4, gas chromatograph with a TCD detector; 5, helium cylinder; 6, transfer tube; 7, sample vial rack.

Weighed alcohol in a small glass ampule was set in a sample vial (22 mL). Fluorocarbon was charged into the vial and weighed with an electronic balance. Then, the weight difference between the fluorocarbon weight W_f and the air weight that replaced by the fluorocarbon W_a was used to determine the overall compositions according to the relation

$$n_f = \frac{W_f - W_a}{M_f - M_a} \tag{1}$$

where M_f and M_a are the molecular weights of fluorocarbon and air, respectively. It should be noted that, for a component in which the molecular weight is close to air, this method could not be applied because the measured weight difference would be extremely small. The sample vial was capped with a special aluminum lid with a butyl rubber seal. Vials were shaken to break the ampule, and then the fluorocarbon was allowed to dissolve into the alcohol. It brought about a reduction in the vial pressure. All vials were set in the autosampler turntable, and after 3 h of equilibrium time, they were injected into the gas chromatograph by the autosampler program.

Calibration. When headspace gas passes into the column for a given time (3 s) as shown in Figure 2, the molar quantity of gas flowing into the column n_i is proportional to the partial pressure p_i because the total pressure was kept constant by pressurizing with helium

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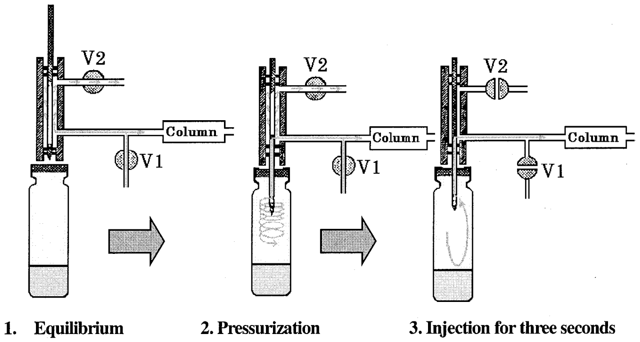

Figure 2. Sampling procedure: V1 and V2, magnetic valves.

Table 1. Mass of the Ampule, Volume of the Vial, and the Specific Volumes of Ampule Glass, Methanol, and Ethanol

V_{vial}	22 mL	v_{methanol}	1.27 mL·g^{-1}
W_{am}	1.6 g	v_{ethanol}	1.27 mL·g^{-1}
v_{am}	0.49 mL·g^{-1}		

for each run. The peak area of gas chromatogram A_i is proportional to the partial pressure as given by

$$p_i = C_iA_i \quad (n_i \propto p_i) \tag{2}$$

where C_i is a response factor of component i determined by calibration. The total pressure P and vapor-phase composition y_i is obtained from

$$P = \sum_{i=1}^{n} p_i \tag{3}$$

$$y_i = p_i/P \tag{4}$$

When the gas phase is assumed to be a perfect gas, the liquid-phase composition can be determined by material balance at temperature T, total pressure P, feed composition z_i, and vapor-phase composition y_i as follows:

$$x_i = \frac{z_i - \theta y_i}{1 - \theta} \tag{5}$$

where θ is the molar ratio of vapor phase n_{vap} to feed n given by

$$\theta = \frac{n_{\mathrm{vap}}}{n} = \frac{PV_{\mathrm{g}}}{RTn} \tag{6}$$

where V_{g} is the headspace volume of the sample vial determined from

$$V_{\mathrm{g}} = V_{\mathrm{vial}} - (W_{\mathrm{al}}v_{\mathrm{al}} + W_{\mathrm{am}}v_{\mathrm{am}}) + \Delta V_{\mathrm{mix}} \tag{7}$$

where W_{al} is the weight of the alcohol. The values of W_{am}, v_{am}, v_{al}, and V_{vial} are listed in Table 1. The volume of mixing ΔV_{mix} in eq 4 was neglected. The headspace volume decreases as the quantity of alcohol in an ampule increases. It was found that the calibration curve shifted when the headspace volume changed, as shown in Figure 3. Headspace gas flows into a column by the pressure difference between the internal pressure of the vial and the ambient pressure, and the molar quantity of the gas is proportional to the pressure difference. The smaller headspace volume results in less vapor being injected into the column and causes the calibration curve to shift. The partial pressure of component i is proportional to both the area and the headspace volume and could be correlated with

$$p_i = (a_1 + a_2)A_i + (a_3 + a_4V_{\mathrm{g}})A_i^2 \tag{8}$$

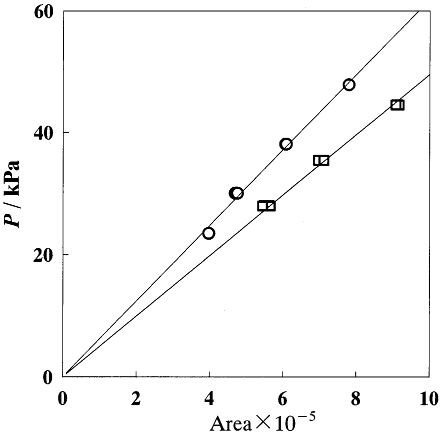

Figure 3. Calibration of methanol: ○, calibration at 10 mL of headspace volume; □, calibration at 3 mL of headspace volume.

Experiments were carried out at temperatures ranging from 303 to 323 K. For each temperature, three sets of vials containing 2.0, 2.5, and 3.0 mL of alcohol were used. The vapor pressures of the alcohols were calculated from the Antoine correlation. For fluorocarbons, three sets of vials containing 2.0, 2.5, and 3.0 mL of glass tips were used. Fluorocarbons were weighed in vials and measured at 313 K. For the case of the perfect gas, the partial pressure of fluorocarbons was determined with

$$p_i = n_iRT/V_{\mathrm{g}} \tag{9}$$

The partial pressure was plotted against the peak area of the gas chromatogram. The present experimental data were correlated by eq 8. The maximum deviation was 2.2% in the liquid phase and 2.1% in the vapor phase. The overall average deviation was 0.8% in alcohol mole fraction and 0.8% in fluorocarbon mole fraction.

Results and Discussion

Vapor−Liquid Equilibria. Table 2 shows experimental data on vapor−liquid equilibria for binary systems of alcohols (methanol or ethanol) + fluorocarbons (HCFC22, HFC32, HFC125, HFC134a, or HFC152a) ranging from 303 to 323 K below atmospheric pressure. The uncertainties of fluorocarbon compositions are estimated to be less than 2% for each phase. Figure 4 shows vapor−liquid equilibria of methanol + chlorodifluoromethane (CFC12) at 303 K.

Solubility. Hildebrand and Scott[5] gave the relation

$$\Delta S_1 = (s_1 - s_1^{\circ}) = R\left(\frac{\partial \ln x_1}{\partial \ln T}\right)_{\mathrm{sat},T} \tag{10}$$

where x_1 is the solubility of a solute gas in the liquid at T, s_1 is the partial molar entropy of a solute, and s_1° is the entropy of a pure solute. Table 1 shows that the solubility of fluorocarbon in alcohols decreased with temperature. So, ΔS_1 can be expected to be negative. As shown in Figure 5, we obtained the values of ΔS_1 from the slope of a straight line. The values are given in Table 3 together with calculated solubility values at 303 K.

Table 2. Experimental Vapor−Liquid Equilibrium Data

T/K	P/kPa	liquid-phase mole fraction x_1	vapor-phase mole fraction y_1	Henry's law constant, H/MPa	T/K	P/kPa	liquid-phase mole fraction x_1	vapor-phase mole fraction y_1	Henry's law constant, H/MPa
Chlorodifluoromethane (HCFC22) + Methanol									
303.0	42.6	0.011 5	0.449	1.66	318.0	72.1	0.011 1	0.375	2.45
	37.8	0.008 80	0.383			72.9	0.011 0	0.373	
308.0	50.7	0.011 2	0.422	1.93	323.0	86.7	0.010 0	0.347	2.99
	50.6	0.011 1	0.423			86.5	0.010 2	0.349	
	45.6	0.008 50	0.362			79.8	0.008 10	0.305	
	44.3	0.008 00	0.353			80.8	0.008 20	0.304	
313.0	64.5	0.010 9	0.395	2.35					
	58.6	0.008 40	0.343						
	59.0	0.008 70	0.340						
Chlorodifluoromethane (HCFC22) + Ethanol									
303.0	32.3	0.016 0	0.645	1.29	318.0	61.2	0.014 5	0.506	2.15
	32.9	0.016 6	0.654			55.1	0.011 9	0.463	
	27.2	0.012 7	0.595			55.4	0.011 9	0.467	
308.0	41.2	0.015 6	0.622	1.52	323.0	66.3	0.013 7	0.524	2.52
	36.1	0.012 9	0.582			59.5	0.011 3	0.475	
313.0	49.7	0.015 1	0.555	1.87					
	49.5	0.014 6	0.561						
Difluoromethane (HFC32) + Methanol									
303.0	56.2	0.007 00	0.582	4.64	323.0	111.0	0.007 00	0.495	7.88
	56.1	0.007 00	0.575			99.4	0.005 60	0.446	
318.0	95.3	0.007 20	0.516	6.93					
	95.0	0.007 00	0.511						
	91.3	0.006 30	0.488						
Difluoromethane (HFC32) + Ethanol									
303.0	59.7	0.010 1	0.798	4.66	313.0	78.6	0.008 80	0.731	6.53
	51.4	0.008 80	0.782		318.0	94.4	0.008 40	0.716	8.13
	53.3	0.009 00	0.788			80.6	0.006 60	0.677	
308.0	70.7	0.009 60	0.776	5.76	323.0	102.0	0.007 20	0.682	9.62
	72.3	0.009 60	0.778			94.7	0.006 50	0.655	
	63.0	0.008 20	0.755						
	63.2	0.008 50	0.758						
Pentafluoroethane (HFC125) + Methanol									
303.0	59.4	0.007 90	0.613	4.60	313.0	99.4	0.007 50	0.518	6.38
	52.1	0.006 50	0.564			98.4	0.007 70	0.525	
	53.1	0.006 50	0.571			88.1	0.006 20	0.473	
308.0	72.7	0.007 80	0.574	5.38		88.7	0.006 20	0.473	
	71.7	0.007 70	0.579		323.0	112.0	0.006 00	0.462	8.68
	63.6	0.006 20	0.522			110.0	0.005 70	0.447	
	64.1	0.006 20	0.526						
Pentafluoroethane (HFC125) + Ethanol									
308.0	64.5	0.011 7	0.752	4.13	323.0	89.1	0.009 50	0.640	5.98
	54.7	0.009 40	0.711			80.5	0.008 30	0.613	
	56.5	0.009 90	0.719						
313.0	67.8	0.009 90	0.712	4.85					
	59.8	0.008 50	0.682						
1,1,1,2-Tetrafluoroethane (HFC134a) + Methanol									
303.0	50.6	0.010 7	0.549	2.58	313.0	70.5	0.009 80	0.473	3.41
	49.6	0.010 4	0.542			70.4	0.009 60	0.471	
	42.4	0.008 00	0.480			47.0	0.007 50	0.535	
308.0	60.9	0.010 0	0.498	3.05	323.0	92.9	0.007 40	0.388	4.83
	54.3	0.007 80	0.442			85.6	0.005 90	0.328	
1,1,1,2-Tetrafluoroethane (HFC134a) + Ethanol									
303.0	35.4	0.010 2	0.748	2.61	313.0	57.7	0.012 3	0.663	3.11
	37.5	0.010 9	0.761			58.6	0.012 5	0.664	
308.0	54.6	0.013 4	0.712	2.88		52.4	0.010 8	0.638	
	45.0	0.010 5	0.659			51.7	0.010 6	0.642	
	43.9	0.009 90	0.655		323.0	75.4	0.010 4	0.580	4.23
						74.9	0.010 1	0.576	
1,1-Difluoroethane (HFC152a) + Methanol									
303.0	47.7	0.010 3	0.521	2.40	318.0	74.3	0.007 40	0.374	3.69
	48.3	0.010 6	0.521			73.9	0.007 50	0.367	
308.0	58.9	0.009 40	0.473	2.90	323.0	94.3	0.009 10	0.391	4.09
	55.1	0.008 20	0.443			89.1	0.007 70	0.358	
313.0	73.2	0.009 60	0.452	3.40					
	69.6	0.008 90	0.429						
	69.1	0.008 50	0.416						
1,1-Difluoroethane (HFC152a) + Ethanol									
303.0	43.4	0.014 1	0.763	2.35	313.0	56.2	0.012 4	0.654	2.96
	35.6	0.011 0	0.727			58.0	0.012 8	0.660	
308.0	54.5	0.013 8	0.708	2.76		49.8	0.010 6	0.620	
	47.5	0.011 7	0.668		323.0	71.2	0.010 7	0.559	3.76
						78.6	0.012 3	0.593	

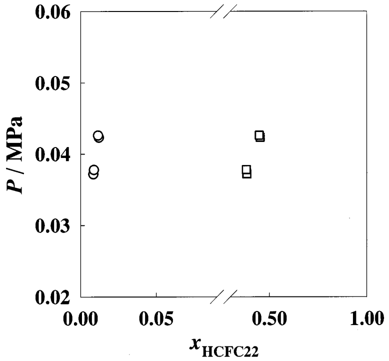

Figure 4. Vapor−liquid equilibria of chlorodifluoromethane (HCFC22) and methanol at 303 K: ○, liquid-phase composition; □, vapor-phase composition.

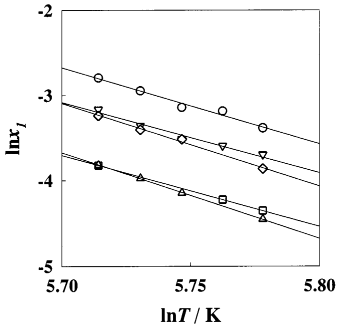

Figure 5. Effect of temperature on the solubility of hydrofluorocarbons in methanol: ○, chlorodifluoromethane (HCFC22); □, difluoromethane (HFC32); △, pentafluoroethane (HFC125); ▽, 1,1,1,2-tetrafluoroethane (HFC134a); ◇, 1,1-difluoroethane (HFC152a); —, Valentiner equation.

Table 3. Entropy and Solubilities of Fluorocarbons in Methanol (303 K and 101 kPa)

compound	$(s_1 - s_1°)$/ J·mol^{-1}·K^{-1}	mole fraction of fluorocarbons in the liquid phase, x_1
chlorodifluoromethane (HCFC22)	−74.04	0.0612
difluoromethane (HFC32)	−69.17	0.0219
pentafluoroethane (HFC125)	−83.51	0.0220
1,1,1,2-tetrafluoroethane (HFC134a)	−81.00	0.0392
1,1-difluoroethane (HFC152a)	−68.90	0.0423

Henry's Law Constants. The Henry's law constant is given by

$$p_1 = H_{12}x_1 \tag{11}$$

where the Henry's law constant H_{12} is expressed in MPa, and x_1 and p_1 are the solute mole fraction in liquid and the partial pressure of a solute, respectively. Figure 6 shows that the Henry's law constant is expressed as a straight line through the origin for the system of HCFC22−methanol. The Henry's law constants listed in Table 2 have estimated uncertainties of 4%. All of the values of the Henry's law constants listed in Table 2 increased with temperature. The temperature dependence was correlated with the Valentiner equation[5]

$$\ln H = a + b/T + c \ln T \tag{12}$$

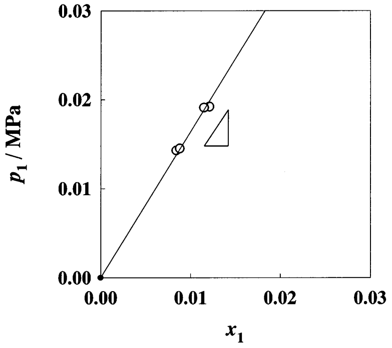

Figure 6. Relationship between the partial pressure and the liquid-phase mole fraction of HCFC22 in methanol at 303 K; ○, experimental data; —, correlated line.

Table 4. Valentiner Constants[a] of Fluorocarbon + Alcohol Systems Ranging from 303 to 323 K

compound	*a*	*b*	*c*
In Methanol			
chlorodifluoromethane (HCFC22)	32.98	−3865	−3.451
difluoromethane (HFC32)	33.19	−3665	−3.425
pentafluoroethane (HFC125)	33.78	−4146	−3.253
1,1,1,2-tetrafluoroethane (HFC134a)	33.41	−4073	−3.331
1,1-difluoroethane (HFC152a)	32.95	−3663	−3.493
In Ethanol			
chlorodifluoromethane (HCFC22)	33.47	−4341	−3.308
difluoromethane (HFC32)	34.23	−4497	−3.125
pentafluoroethane (HFC125)	32.92	−3519	−3.501
1,1,1,2-tetrafluoroethane (HFC134a)	32.66	−3483	−3.543
1,1-difluoroethane (HFC152a)	32.50	−3357	−3.598

[a] $\ln(H/\mathrm{MPa}) = a + b/(T/\mathrm{K}) + c \ln(T/\mathrm{K})$.

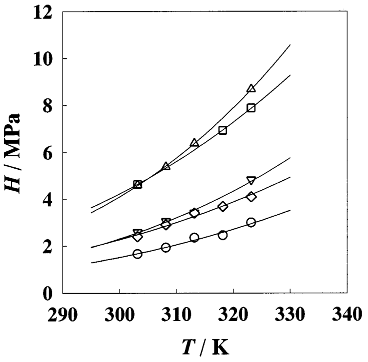

Figure 7. Effect of temperature on the Henry's law constants of chlorodifluoromethane (HCFC22), difluoromethane (HFC32), pentafluoroethane (HFC125), 1,1,1,2-tetrafluoroethane (HFC134a), and 1,1-difluoroethane (HFC152a) in methanol: ○, chlorodifluoromethane (HCFC22); □, difluoromethane (HFC32); △, pentafluoroethane (HFC125); ▽, 1,1,1,2-tetrafluoroethane (HFC134a); ◇, 1,1-difluoroethane (HFC152a); —, Valentiner eq.

The above coefficients are shown in Table 4. Figures 7 and 8 show the Henry's law constants of fluorocarbons in methanol and ethanol, respectively. The Henry's law constants of fluorocarbons in methanol were compared with the experimental data of our previous work.[4] The overall average difference was 7.1%, as shown in Figure 9.

Conclusion

This work shows that the headspace method can be successfully applied to Henry's law constant measurements. The headspace method is quite rapid and flexible when compared with the conventional method. Vapor−liquid equilibria were measured for 10 binary fluorocarbon + alcohol systems ranging from 303 to 323 K below atmospheric pressure. Negative values of Δs_1 were obtained because the solubility of fluorocarbons in alcohols decreases with an increase in the temperature, as shown by our

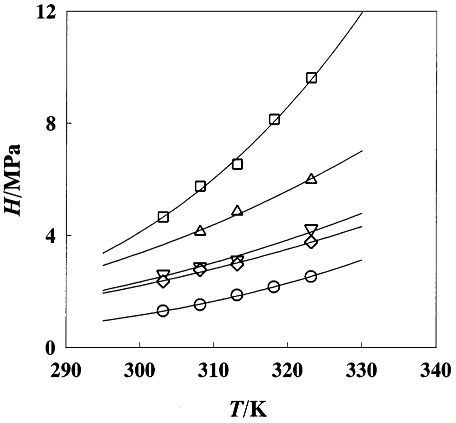

Figure 8. Effect of temperature on the Henry's law constants of chlorodifluoromethane (HCFC22), difluoromethane (HFC32), pentafluoroethane (HFC125), 1,1,1,2-tetrafluoroethane (HFC134a), and 1,1-difluoroethane (HFC152a) in ethanol: ○, chlorodifluoromethane (HCFC22); □, difluoromethane (HFC32); △, pentafluoroethane (HFC125); ▽, 1,1,1,2-tetrafluoroethane (HFC134a); ◇, 1,1-difluoroethane (HFC152a); —, Valentiner eq

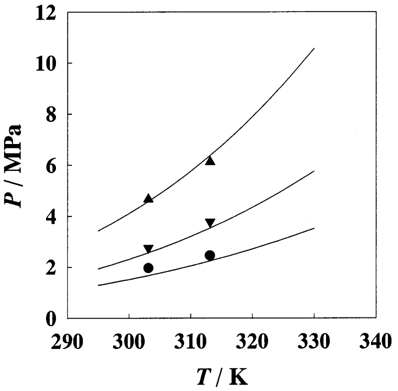

Figure 9. Henry's law constants comparison between this work and work of Takenouchi et al.:[4] ●, chlorodifluoromethane (HCFC22, Takenouchi et al.[4]); ▲, pentafluoroethane (HFC125, Takenouchi et al.[4]); ▼, 1,1,1,2-tetrafluoroethane (HFC134a, Takenouchi et al.[4]); —, Valentiner equation (this work).

previous works.[4] From the experimental data, the Henry's law coefficients of HCFC22, HFC32, CFC115, HFC125, HFC134a, and HFC152a in methanol and ethanol were obtained. The values could be correlated with the Valentiner equation. The solubility of fluorocarbons derived from ethane in both methanol and ethanol increased as the number of hydrogen atoms in the molecule increased.

Nomenclature

A_i = peak area of a component
C_i = proportionality constant
M_a = molecular mass of air
M_f = molecular mass of fluorocarbon
n_f = molar mass of fluorocarbon
n = total molar mass
n_{vap} = molar mass of the vapor phase
P = total pressure
P_i = partial pressure
R = universal gas constant
s_i = partial molar entropy of a solute
s_i° = entropy of pure solute
T = temperature
v_{al} = specific volume of the alcohol
v_{am} = specific volume of the ampule
V_g = volume of the headspace gas
V_{vial} = volume of the vial
W_a = mass of air
W_{al} = mass of alcohol
W_{am} = mass of an ampule
W_f = mass of fluorocarbon gas
x_i = liquid-phase mole fraction
y_i = vapor-phase mole fraction
ΔS_i = dissolution entropy
ΔV_{mix} = volume of mixing
θ = ratio of vapor to liquid

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