

# Isothermal Vapor–Liquid Equilibrium Data for the 1,1,2,2-Tetrafluoroethene + 1,1,2,3,3,3-Hexafluoroprop-1-ene Binary System: Measurement and Modeling from (248 to 283) K

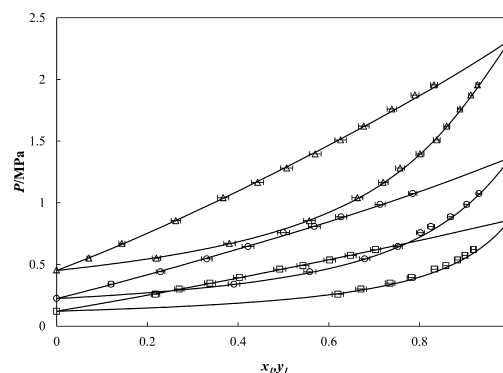
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**Abstract:** Isothermal vapor–liquid equilibrium data are presented for the 1,1,2,2-tetrafluoroethylene and 1,1,2,3,3,3-hexafluoroprop-1-ene binary system at (248.14, 263.01, and 282.89) K, with pressures ranging from (0.12 to 2.35) MPa. An apparatus based on the “static–analytic” method, equipped with a movable rapid online sampler–injector (ROLSI), was used to undertake the measurements. The combined expanded uncertainties are estimated at 0.11 K, 4 kPa, and 0.012 and 0.009 for the temperature, pressure, and the equilibrium liquid and vapor mole fractions, respectively. The experimental data were correlated with the Peng–Robinson equation of state using the Mathias–Copeman  $\alpha$  function, together with the Wong–Sandler mixing rule utilizing the nonrandom two-liquid activity coefficient model.



## Introduction

South Africa has abundant fluorospar deposits. Consequently, there are initiatives from the South African Department of Science and Technology (DST) to investigate means of beneficiating these reserves. One example of beneficiation is the production of various fluoropolymers, of which both tetrafluoroethylene (TFE) and hexafluoropropylene (R-1216) monomers are core precursors. TFE and R-1216 are produced together via the pyrolysis of polytetrafluoroethylene. However, for the production of various fluoropolymers, pure constituents are required. Distillation is normally used to purify TFE and R-1216. In order for the optimal conditions for distillation to be determined, accurate vapor–liquid data are required. We have previously reported high-pressure vapor–liquid equilibrium (VLE) data for binary systems involving R-1216 with either propylene,<sup>1</sup> ethane,<sup>2</sup> 1-butene,<sup>3</sup> ethylene,<sup>4</sup> carbon dioxide,<sup>5</sup> or 2,2-dichloro-1,1,1-trifluoroethane,<sup>5</sup> and the binary system of TFE and 1,1,2,2,3,3,4,4-octafluorocyclobutane.<sup>6</sup> To the best of our knowledge, VLE data for the binary system of TFE and R-1216 has not been published in open literature. Additionally, methods used to predict VLE such as UNIFAC and its constituents<sup>7–9</sup> are not viable in this case, as the molecules of TFE and R-1216 cannot be constructed using the predefined functional groups. In this study, isothermal vapor–liquid equilibrium data for the binary system of TFE and R-1216 were measured at (248.1, 263.0, and 282.9) K. A “static–analytic” apparatus was used to measure the VLE data. The experimental data were correlated using the Peng–Robinson (PR)<sup>10</sup> equation of state (EOS) with the

Mathias–Copeman (MC)<sup>11</sup>  $\alpha$  function, coupled with the Wong–Sandler (WS)<sup>12</sup> mixing rules and the nonrandom two-liquid (NRTL)<sup>13</sup> activity coefficient model.

## Experimental section

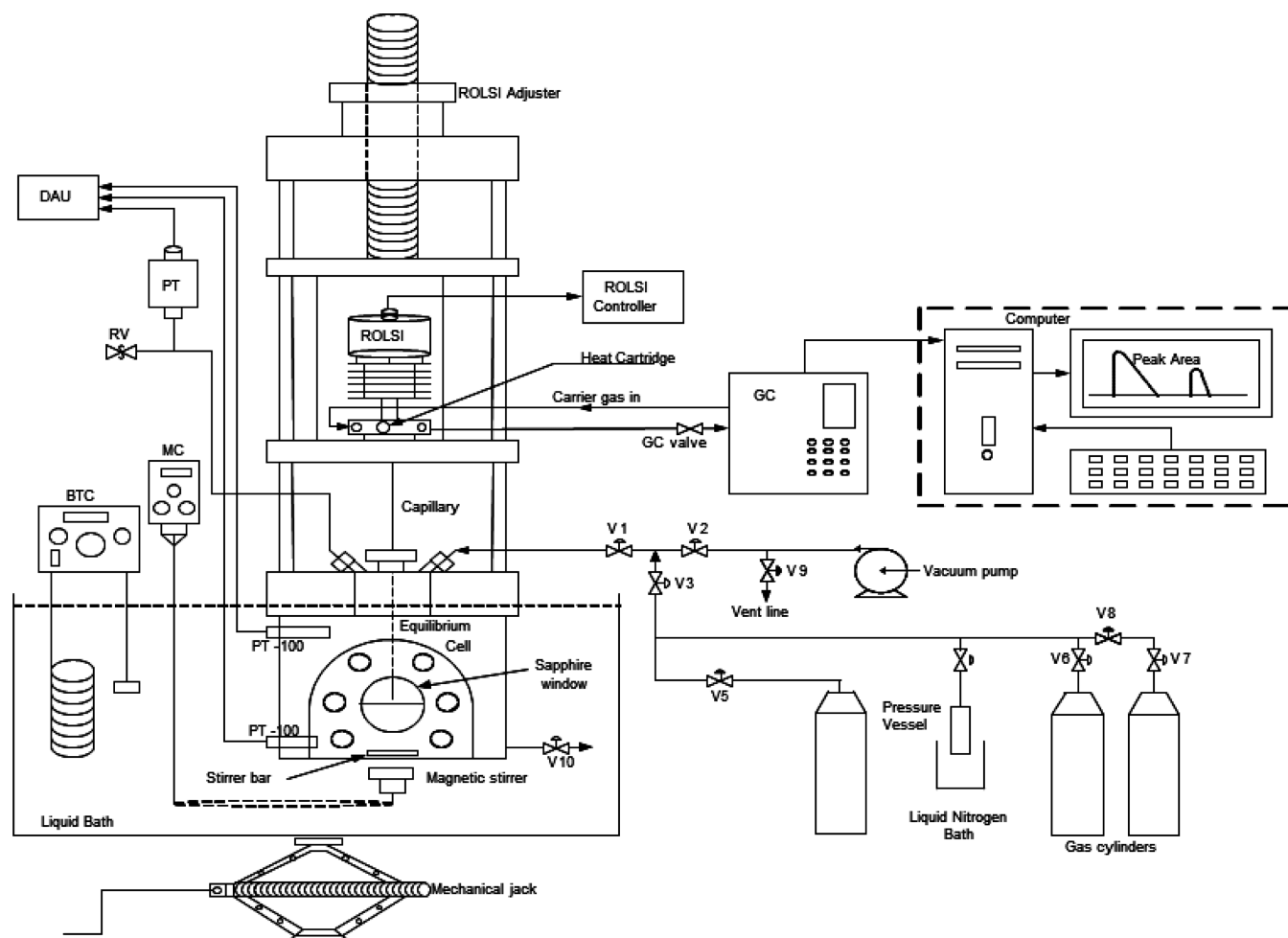
**Materials.** TFE (C<sub>2</sub>F<sub>4</sub>) was produced in-house at The South African Nuclear Energy Corporation (NECSA) via a laboratory-scale distillation process. To prevent autopolymerization of the TFE, NECSA limited the TFE cylinder pressure to 0.18 MPa. R-1216 (C<sub>3</sub>F<sub>6</sub>) was also produced in-house by Pelchem, a subsidiary of NECSA. The supplier stated purities for the chemicals listed in Table 1 were confirmed by gas chromatography (GC) analysis. No significant purities beyond the supplier specifications were observed, as the GC peak areas values greater than the supplier stated purities. Apart from degassing, no further purification of the chemicals was undertaken. The critical temperatures ( $T_c$ ), critical pressures ( $P_c$ ), and acentric factors, obtained from literature,<sup>14,15</sup> for both pure components are listed in Table 1, including the Chemical Abstract Service (CAS) numbers, and purities as stated by the suppliers.

**Experimental Apparatus.** The experimental data were measured using an apparatus based on the “static–analytic” method which was fitted with a movable rapid online sampler–injector

**Table 1. Critical Properties and Other Relevant Information for the Materials and the Mathias–Copeman Parameters for the Pure Components**

	CAS no.	purity <sup>a</sup>	critical properties			Mathias–Copeman coefficients		
			$T_c$ /K	$P_c$ /MPa	$\omega$	$c_1$	$c_2$	$c_3$
TFE <sup>14</sup>	116-14-3	0.998	306.45	3.944	0.2230	0.5939	0.7535	0.3769
R-1216 <sup>23</sup>	116-15-4	0.999	358.9	3.136	0.3529	0.8872	-0.1307	0.7628

<sup>a</sup>Supplier purity (mole fraction) stated by the South African Nuclear Energy Corporation.



**Figure 1.** A schematic of the apparatus:<sup>6</sup> BTC, bath temperature controller; DAU, data acquisition unit; GC, gas chromatograph; MC, mechanical circulator; PT, pressure transducer; RV, relief valve;  $V_i$ , valve.

(ROLSI)<sup>16</sup> to sample both the liquid and the vapor phases at equilibrium. Figure 1 shows a schematic of the experimental setup. The equilibrium cell (approximately 40 cm<sup>3</sup> in volume) was submerged into a temperature regulated liquid bath containing an ethylene glycol and water solution. The mixture within the equilibrium cell was agitated via a PTFE-coated stirrer bar which was magnetically coupled to an externally driven rare-earth magnet. The temperature of the cell was monitored by two platinum resistance thermometer (Pt-100) probes situated at the top and base of the equilibrium cell. The Pt-100 probes were calibrated against a reference thermometer (CTH 6500, WIKA) calibrated directly by WIKA Instruments. The reference probe was stated to have a maximum internal uncertainty of 0.02 K. The measuring pressure transmitter (WIKA P-10, (0 to 10) MPa) was calibrated against a reference pressure transmitter (CPT 6000, WIKA) previously calibrated by WIKA Instruments. The reference pressure transmitter was

stated to have a maximum uncertainty of 0.02 kPa. Pressure and temperature readings were recorded via an Agilent Data Acquisition Unit (34970A) linked via a RS-232 connection to a desktop PC.

Samples of both the liquid and vapor phases at equilibrium, withdrawn by the ROLSI, were transferred directly to and analyzed with a Shimadzu G-17A GC fitted with a thermal conductivity detector (TCD). The GC was equipped with a Porapak Q column (length: 3 m, diameter: 1/8 in., 80/100 mesh) which was maintained at 503 K. Helium gas was used as the carrier gas with a total flow rate of 25 mL·min<sup>-1</sup>. The TCD response was calibrated by injecting known volumes (direct injection method) for each of the pure components.

**Experimental Procedure.** The equilibrium cell and all associated lines were thoroughly evacuated before component loading, to ensure the removal of any residual components potentially retained in the sealing media. The heavier component,

namely, R-1216, was initially loaded into the equilibrium cell by inducing a temperature gradient between the R-1216 cylinder and the equilibrium cell (lower temperature). Approximately 15 cm<sup>3</sup> of liquid R-1216 was charged into the equilibrium cell. The R-1216 within the cell was degassed via periodic vapor withdrawal. At different temperature intervals the vapor pressure of R-1216 was recorded when the temperature and pressure stabilized to within the measuring precision of the respective instruments for at least 10 min.

Following the vapor pressure measurements, TFE was charged into the equilibrium cell. Liquid TFE was transferred into the equilibrium cell from a small pressure vessel (about 10 cm<sup>3</sup>) which was mildly heated. The TFE was loaded in this manner to prevent autopolymerization and autodecomposition.<sup>6</sup>

The equilibrium mixture was rapidly agitated at constant temperature; thermodynamic equilibrium was assumed to be achieved when the total pressure recorded stabilized to within the measurement uncertainty for a period of at least 10 min. At equilibrium, the liquid and vapor phases were individually sampled via the ROLSI, and the equilibrium compositions were determined by GC analysis. The operating times of the ROLSI were set to prevent disturbance of the equilibrium condition due to potential volume changes and furthermore to ensure that the sample sizes withdrawn at equilibrium were within the calibration range of the TCD. At least five reproducible samples were withdrawn at equilibrium for each phase. The entire phase envelope was covered by increasing the concentration of TFE within the equilibrium cell in a stepwise manner and measuring the successive equilibrium mixtures.

### Experimental uncertainty

The experimental uncertainties in this work were calculated by the method outlined by NIST (National Institute of Standards and Technology).<sup>17,18</sup> A detailed overview of the calculation route used in relation to VLE measurements can be found in the thesis of Soo<sup>19</sup> and Nelson.<sup>20</sup> The combined expanded uncertainties for both the pressure and the temperature measurements were estimated by taking into account the standard uncertainties inherent to both the pressure and temperature measurement standards, correlation polynomials, and the repeatability of the measurements. The combined expanded uncertainties for composition were calculated by accounting for standard uncertainties inherent to correlation polynomials, repeatability, and the calibration method.

Consider the standard uncertainty due to the calibration method for the number of moles, that is, the direct injection method. Using the ideal gas law, the number of moles is influenced by the pressure, temperature, and volume of the gas injected into the GC. Thus, the standard uncertainty of the number of moles,  $u_{ig}(n_i)$ , injected into the GC is:

$$u_{ig}(n_i) = \left\{ \left[ \left( \frac{\partial n_i}{\partial P} \right)_{V,T} u_{ig}(P) \right]^2 + \left[ \left( \frac{\partial n_i}{\partial V} \right)_{P,T} u_{ig}(V) \right]^2 + \left[ \left( \frac{\partial n_i}{\partial T} \right)_{P,V} u_{ig}(T) \right]^2 \right\}^{1/2} \quad (1)$$

where  $u_{ig}(P)$ ,  $u_{ig}(V)$ , and  $u_{ig}(T)$  are the uncertainties related to the pressure, volume, and temperature, respectively, of

component  $i$  injected into the gas chromatograph. Both the uncertainty due to the calibration method and the correlation polynomials are derived in terms of the number of moles and can be converted to the uncertainty in composition (for a binary mixture) via:

$$u(x_i) = \sqrt{\left[ \left( \frac{\partial x_i}{\partial n_i} \right)_{n_j} u(n_i) \right]^2 + \left[ \left( \frac{\partial x_i}{\partial n_j} \right)_{n_i} u(n_j) \right]^2} \quad (2)$$

Table 2 lists the standard uncertainties influencing the measurements in this work. In case of repeatability of

**Table 2. Standard Uncertainties,  $u$ , of Pressure,  $P$ , Temperature,  $T$ , Volume,  $V$ , and Mole Numbers,  $n$ , Influencing the Measurands of this Work**

source of uncertainty	estimate	distribution	influence
standard pressure transmitter (kPa)	0.02	rectangular	$P$
standard temperature probe (K)	0.02	rectangular	$T$
correlation for $P$ (kPa)	3.5	rectangular	$P$
correlation for $T$ (K)	0.09	rectangular	$T$
correlation for $n_i$ of TFE	2.5	rectangular	$x, y$
correlation for $n_i$ of HFP	2.0	rectangular	$x, y$
correlation for $n_i$ of TFE (dilute region)	3.0	rectangular	$x, y$
correlation for $n_i$ of HFP (dilute region)	3.0	rectangular	$x, y$
$V$ of injected gas from syringe <sup>a</sup> , $u_{ig}(V)$	2%	rectangular	$x, y$
$T$ of injected gas from syringe <sup>a</sup> , $u_{ig}(T)$ (K)	2	rectangular	$x, y$
$P$ of injected gas from syringe <sup>a</sup> , $u_{ig}(P)$ (kPa)	1	rectangular	$x, y$

<sup>a</sup>Uncertainties inherent to the direct injection method, estimated from the ideal gas law.

the measurements, the measured temperatures, pressures, and compositions were treated as Gaussian distributions (i.e., type A). The combined expanded uncertainty for the relative volatility,  $U(\alpha_{ij})$ , was calculated using the combined standard uncertainties for composition in both the liquid and the vapor phases. The combined standard uncertainty in the relative volatility,  $u(\alpha_{ij})$ , can be calculated from:

$$u(\alpha_{ij}) = \sqrt{\left[ \left( \frac{\partial \alpha_{ij}}{\partial x_i} \right)_{y_i} u(x_i) \right]^2 + \left[ \left( \frac{\partial \alpha_{ij}}{\partial y_i} \right)_{x_i} u(y_i) \right]^2} \quad (3)$$

where  $u(x_i)$  and  $u(y_i)$  are the standard uncertainties for  $x$  and  $y$ , respectively; both were treated as rectangular distributions. The combined standard uncertainties were converted to the combined expanded uncertainties using  $k = 2$ , defining an interval having a level of confidence of approximately 95 %. The combined expanded uncertainties for the experimental variables, averaged over all points, are estimated as:  $U(T) = 0.11$  K,  $U(P) = 0.004$  MPa,  $U(x_1) = 0.012$ , and  $U(y_1) = 0.009$ . It is noted that, although vapor phase composition is in general more difficult to measure than that the liquid phase, the uncertainties estimated for liquid-phase composition are on average higher than those of the vapor phase. This is due to the fact that sample repeatability had a very small contribution toward the final estimation of the uncertainty for composition. Uncertainties for both the liquid and the vapor phase compositions for each individual data point are listed in Table 4.

## Correlations

The model parameters were fitted using Aspen Plus version 7.0.<sup>21</sup> The vapor pressure data were correlated using the PR EOS:

$$P = \frac{RT}{V_m - b} - \frac{a(T)}{V_m(V_m + b) + b(V_m - b)} \quad (4)$$

where  $P$  is the pressure,  $R$  is the universal gas constant,  $T$  is the temperature,  $V_m$  is the molar volume, and  $b$  is a function of  $T_c$  and  $P_c$ .  $a(T)$  is described by  $T_c$ ,  $P_c$ , and in this work the MC  $\alpha$  function:

$$\alpha_i(T) = [1 + c_{1,i}(1 - \sqrt{T_{R,i}}) + c_{2,i}(1 - \sqrt{T_{R,i}})^2 + c_{3,i}(1 - \sqrt{T_{R,i}})^3]^2 \quad (5)$$

where  $T_R$  is the reduced temperature. The three adjustable parameters ( $c_i$ ) of the MC  $\alpha$  function fitted to the experimental vapor pressure data of R-1216 are presented in Table 1; the MC parameters for TFE were referenced from a previous paper.<sup>6</sup> The experimental VLE data were correlated using the PR-EOS with the MC  $\alpha$  function, coupled with the WS mixing rule using the NRTL activity coefficient model. The WS mixing rule is:

$$b_m = \frac{RT \sum_i \sum_j x_i x_j [b_{ij} - (a_{ij}/RT)]}{RT - [\sum_i x_i (a_i/b_i) + (G^E/C)]} \quad (6)$$

where  $G^E$  is the excess Gibbs energy described by the NRTL activity coefficient model and  $x$  is the liquid phase composition, with:

$$\left(b_{ij} - \frac{a_{ij}}{RT}\right) = \frac{1}{2} \left[ \left(b_i - \frac{a_i}{RT}\right) + \left(b_j - \frac{a_j}{RT}\right) \right] (1 - k_{ij}) \quad (7)$$

and

$$a_m = b_m \left( \sum_i x_i \frac{a_i}{b_i} + \frac{G^E}{C} \right) \quad (8)$$

where  $C = -1/(2^{1/2}) \ln(1 + 2^{1/2})$  for the PR EOS and  $k_{ij}$  is the binary interaction parameter. The NRTL activity coefficient model is:

$$\frac{G^E}{RT} = x_i x_j \left( \frac{\tau_{ji} G_{ji}}{x_i + x_j G_{ji}} + \frac{\tau_{ij} G_{ij}}{x_j + x_i G_{ij}} \right) \quad (9)$$

where

$$G_{ij} = \exp(-\alpha_{ij} \tau_{ij}) \quad (10)$$

In Aspen Plus the binary interaction parameters can be defined as:

$$\tau_{ij} = a_{ij} + b_{ij}/T \quad (11)$$

The interaction parameters ( $k_{ij}$ ,  $\tau_{ij}$ ,  $\tau_{ji}$ ) were adjusted to the VLE data using the Britt–Luecke algorithm<sup>22</sup> and a maximum likelihood objective function ( $F$ ) presented in eq 12.  $\alpha_{ij}$  is fixed at 0.3 as recommended by Renon and Prausnitz.<sup>13</sup> The objective function ( $F$ ) used was:

$$F = \sum_{n=1}^{NDG} W_n \sum_{i=1}^{NP} \left[ \left( \frac{T_{e,i} - T_{m,i}}{\sigma_{T,i}} \right)^2 + \left( \frac{P_{e,i} - P_{m,i}}{\sigma_{P,i}} \right)^2 + \sum_{j=1}^{NC-1} \left( \frac{x_{e,i,j} - x_{m,i,j}}{\sigma_{x,i,j}} \right)^2 + \sum_{j=1}^{NC-1} \left( \frac{y_{e,i,j} - y_{m,i,j}}{\sigma_{y,i,j}} \right)^2 \right] \quad (12)$$

where NDG is the number of data groups used in the data regression;  $w_n$  is the weight of the data group; NP is the number of data points; NC is the number of components;  $T$ ,  $P$ ,  $x$ , and  $y$  are the temperature, pressure, and liquid and vapor mole fractions, respectively; e and m are the experimental and modeled data, respectively;  $\sigma$  is the standard deviation.

The BIAS (eq 13) and MRD (eq 14) are used to statistically analyze the quality of the model fit.

$$\text{Bias}(\theta)\% = \frac{100}{n} \sum_n \left( \frac{\theta_{\text{exp}} - \theta_{\text{cal}}}{\theta_{\text{exp}}} \right) \quad (13)$$

$$\text{MRD}(\theta)\% = \frac{100}{n} \sum_n \left| \frac{\theta_{\text{exp}} - \theta_{\text{cal}}}{\theta_{\text{exp}}} \right| \quad (14)$$

where  $n$  is the number of data points, and  $\theta$  is the either  $T$ ,  $P$ ,  $x$ , or  $y$ .

## Results and Discussion

Table 3 lists the experimental pure-component vapor pressure data for R-1216 and compares it to literature<sup>23</sup> values. Table 3

**Table 3. Comparison of the Saturated Pressure,  $P$ , and Temperature,  $T$ , of TFE and R-1216 to Literature and Modeled Data (Peng–Robinson Equation of State with the Mathias–Copeman  $\alpha$  Function)<sup>a</sup>**

T/K	experimental	literature		model	
	$P_{\text{exp}}/\text{MPa}$	$P_{\text{lit}}/\text{MPa}$	$ \Delta P ^b/\text{MPa}$	$P_{\text{mod}}/\text{MPa}$	$ \Delta P ^b/\text{MPa}$
TFE <sup>c</sup>					
248.20	0.864	0.868	0.004	0.864	0.000
253.34	1.017	1.023	0.006	1.017	0.000
263.18	1.367	1.375	0.008	1.367	0.000
273.14	1.804	1.810	0.006	1.804	0.000
283.19	2.340	2.338	0.002	2.339	0.001
R-1216 <sup>d</sup>					
248.14	0.120	0.119	0.001	0.122	0.001
253.27	0.150	0.149	0.001	0.151	0.001
263.01	0.225	0.223	0.002	0.224	0.002
282.92	0.452	0.455	0.003	0.452	0.000
292.76	0.617	0.619	0.002	0.615	0.002
303.07	0.832	0.835	0.003	0.830	0.002
313.38	1.099	1.103	0.004	1.097	0.002
323.06	1.408	1.408	0.000	1.403	0.005
334.96	1.863	1.867	0.004	1.864	0.001
345.26	2.345	2.350	0.005	2.349	0.004
352.78	2.757	2.761	0.004	2.758	0.001

<sup>a</sup> $U(T) = 0.11$  K,  $U(P) = 4$  kPa. <sup>b</sup> $|\Delta P| = |P_{\text{exp}} - P_{\text{lit}}|$  or  $\Delta P = |P_{\text{exp}} - P_{\text{mod}}|$ , where  $P_{\text{exp}}$ ,  $P_{\text{lit}}$ , and  $P_{\text{mod}}$  are the experimental, literature, and modeled vapor pressures, respectively. <sup>c</sup>Reference vapor pressure data for TFE predicted using Antoine parameters provided by Yaws.<sup>24</sup> <sup>d</sup>Reference vapor data for R-1216 sourced from Coquelet et al.,<sup>23</sup> the data was modeled and predicted at our experimental temperatures via the PR equation of state and the MC  $\alpha$  function.

**Table 4. Experimental Pressure,  $P$ , Liquid-Phase Composition,  $x$ , and Vapor-Phase Composition,  $y$ , Data for the Binary System TFE (1) + R-1216 (2) at Temperatures,  $T = (248.14, 263.01, \text{ and } 282.89) \text{ K}$ , Including the Combined Expanded Uncertainties,  $U^a$**

$P/\text{MPa}$	$x_1$	$y_1$	$U(x_1)$	$U(y_1)$
$T/\text{K} = 248.14$				
0.1202	0.000	0.000		
0.2581	0.218	0.620	0.009	0.013
0.3004	0.270	0.671	0.011	0.012
0.3484	0.338	0.735	0.012	0.010
0.3944	0.403	0.782	0.013	0.009
0.4616	0.492	0.833	0.013	0.008
0.4899	0.543	0.858	0.013	0.007
0.5365	0.602	0.884	0.013	0.006
0.5734	0.648	0.900	0.012	0.006
0.6200	0.703	0.919	0.011	0.005
$T/\text{K} = 263.01$				
0.2246	0.000	0.000		
0.3402	0.120	0.391	0.006	0.013
0.4408	0.229	0.558	0.010	0.013
0.5459	0.331	0.679	0.012	0.012
0.6453	0.422	0.752	0.013	0.010
0.7576	0.500	0.802	0.013	0.009
0.8078	0.568	0.825	0.013	0.008
0.8863	0.627	0.868	0.013	0.006
0.9866	0.713	0.904	0.011	0.005
1.0755	0.785	0.931	0.009	0.004
$T/\text{K} = 282.89$				
0.4561	0.000	0.000		
0.5510	0.071	0.220	0.004	0.009
0.6710	0.144	0.381	0.007	0.013
0.8547	0.263	0.557	0.010	0.013
1.0414	0.367	0.663	0.012	0.012
1.1659	0.443	0.720	0.013	0.011
1.2821	0.507	0.757	0.013	0.010
1.3965	0.570	0.801	0.013	0.009
1.5094	0.626	0.838	0.013	0.007
1.6220	0.677	0.860	0.012	0.007
1.7599	0.739	0.889	0.010	0.006
1.8736	0.790	0.913	0.009	0.005
1.9564	0.832	0.928	0.007	0.004

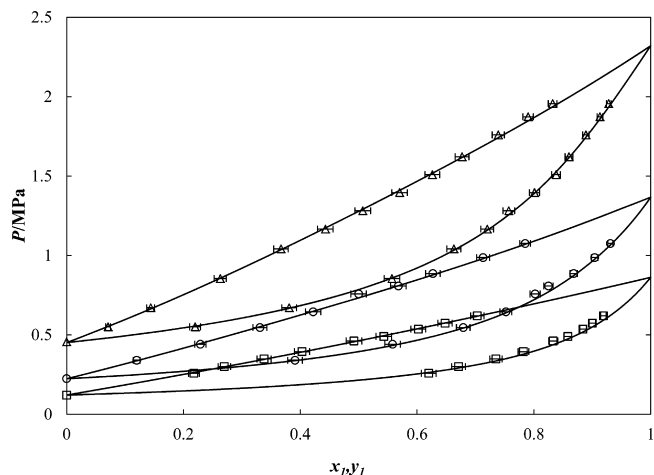
<sup>a</sup> $U(T) = 0.11 \text{ K}$ ,  $U(P) = 4 \text{ kPa}$ .

**Table 5. Fitted Binary Interaction Parameters for the Binary System TFE (1) + R-1216 (2) Using the PR-EOS with the MC  $\alpha$  Function Coupled with the WS Mixing Rules and the NRTL Activity Coefficient Model**

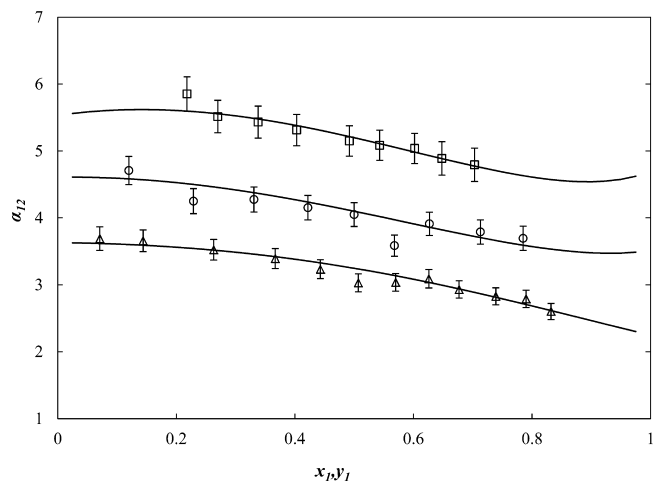
$T/\text{K}$	$a_{12}^a$	$a_{21}^a$	$k_{12}$
248.14	5.471	-0.028	-0.373
263.01	5.048	-0.223	-0.254
282.89	4.581	-0.652	-0.031
$T/\text{K}$	$b_{12}^b$	$b_{21}^b$	$k_{12}$
248.14, 263.01, and 282.89	-688.989	-33.049	-0.105

<sup>a</sup> $\tau_{ij} = a_{ij}$ , parameters fitted to each isotherm individually. <sup>b</sup> $\tau_{ij} = b_{ij}/T$ , parameters fitted to all isotherms simultaneously.

also shows a comparison between the experimental and the calculated vapor pressure data for R-1216 using the PR EOS with the MC  $\alpha$  function. The R-1216 vapor pressure data are in good agreement with literature data<sup>23</sup> for the entire temperature



**Figure 2.** Plot of the  $P$ - $x$ - $y$  data for the binary system of TFE (1) + R-1216 (2):  $\Delta$ ,  $T = 282.89 \text{ K}$ ;  $\circ$ ,  $T = 263.01 \text{ K}$ ;  $\square$ ,  $T = 248.14 \text{ K}$ ; —, model. Error bars are presented for  $U(x)$  and  $U(y)$  only.



**Figure 3.** Plot of the relative volatility ( $\alpha_{12}$ ) for the binary system of TFE (1) + R-1216 (2):  $\Delta$ ,  $T = 282.89 \text{ K}$ ;  $\circ$ ,  $T = 263.01 \text{ K}$ ;  $\square$ ,  $T = 248.14 \text{ K}$ ; —, model. Error bars are presented for  $U(\alpha_{12})$  only.

range studied. A satisfactory fit of the vapor pressure data for R-1216 was achieved with the MC  $\alpha$  function.

The experimental  $P$ - $x$ - $y$  data are listed in Table 4. The adjusted binary interaction parameters for the WS mixing rules and NRTL activity coefficient are shown in Table 5. The experimental and predicted VLE data using the regressed model parameters are illustrated in Figure 2. The experimental and predicted relative volatilities are presented in Figure 3. The MRD and BIAS are listed in Table 6; in the first case each isotherm was regressed individually using scalar parameters, and in the second case all isotherms were regressed simultaneously using temperature-dependent parameters. The aforementioned model combination provides a good fit to the experimental data; however, it is clear that the isothermal data is depicted with higher accuracy using the scalar parameters regressed for each isotherm individually. However, the temperature-dependent parameters would be more useful for design purposes.

The plot of the relative volatility (Figure 3) provides some useful information. In the figure it can be seen that two data points of the 263.01 K isotherm and a single data point of the 282.89 K isotherm deviate from the modeled data beyond the stated experimental uncertainty. This indicates that the



**Table 6. Relative Deviations, Bias, and MRD between the Experimental and Model Data Using the PR-EOS, MC  $\alpha$  Function Coupled with the WS Mixing Rules, and the NRTL Activity Coefficient Model for the Binary System TFE (1) + R-1216 (2) at (248.14, 263.01, and 282.89) K**

scalar parameters ( $\tau_{12} = a_{12}$ ) <sup>a</sup>								
T/K	MRD(T)%	Bias(T)%	MRD(P)%	Bias(P)%	MRD(x)%	Bias(x)%	MRD(y)%	Bias(y)%
248.14	0.07	0.00	0.05	0.00	0.03	0.00	0.28	-0.09
263.01	0.10	0.02	0.10	-0.02	0.08	-0.01	0.93	0.36
282.89	0.08	0.02	0.10	-0.03	0.05	-0.02	0.58	-0.03
temperature-dependent parameters ( $\tau_{12} = b_{12}/T$ ) <sup>b</sup>								
248.14	0.09	0.05	0.06	-0.02	0.05	-0.03	0.82	0.60
263.01	0.11	-0.04	0.11	0.05	0.10	-0.08	1.34	1.30
282.89	0.10	0.05	0.13	-0.08	0.04	0.02	0.67	-0.61

<sup>a</sup>Scalar parameters fitted to each isotherm individually. <sup>b</sup>Temperature-dependent parameters fitted to all isotherms simultaneously.

forementioned data points are potentially erroneous, but it is inconclusive that the data is incorrect as the relative volatility results are model-dependent.

## Conclusions

Isothermal VLE data for the TFE and R-1216 binary system at (248.14, 263.01, and 282.89) K were measured using an apparatus using the “static-analytic” method. The combined expanded uncertainties for the temperature, pressure, and the equilibrium liquid and vapor mole fractions are 0.11 K, 4 kPa, and 0.012 and 0.009, respectively. The experimental data were correlated using the PR EOS with the MC  $\alpha$  function, coupled with the WS mixing rules and the NRTL activity coefficient model. The model provides a good fit to the experimental data to within the experimental uncertainty.

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### Notes

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## References

- (1) Coquelet, C.; Valtz, A.; Naidoo, P.; Ramjugernath, D.; Richon, D. Isothermal Vapor-Liquid Equilibrium Data for the Hexafluoropropylene (R1216) + Propylene System at Temperatures from (263.17 to 353.14) K. *J. Chem. Eng. Data* **2010**, *55*, 1636–1639.
- (2) Subramoney, S. C.; Valtz, A.; Coquelet, C.; Richon, D.; Naidoo, P.; Ramjugernath, D. Vapor-Liquid Equilibrium Measurements and Modeling for the Ethane (R-170) + 1,1,2,3,3,3-Hexafluoro-1-propene (R-1216) Binary System. *J. Chem. Eng. Data* **2012**, *57*, 2947–2955.
- (3) Subramoney, S. C.; Valtz, A.; Coquelet, C.; Richon, D.; Naidoo, P.; Ramjugernath, D. Experimental vapour-liquid equilibrium data and modeling for binary mixtures of 1-butene with 1,1,2,3,3,3-hexafluoro-1-propene, 2,2,3-trifluoro-3-(trifluoromethyl)oxirane, or difluoromethane. *J. Chem. Thermodyn.* **2013**, *61*, 18–26.
- (4) Subramoney, S. C.; Courtial, X.; Naidoo, P.; Coquelet, C.; Richon, D.; Ramjugernath, D. Isothermal vapor-liquid equilibrium data for the ethylene + 1,1,2,3,3,3-hexafluoro-1-propene binary system between 258 and 308 K at pressures up to 4.56 MPa. *Fluid Phase Equilib.* **2013**, *353*, 7–14.
- (5) Nelson, W. M.; Subramoney, S. C.; Valtz, A.; Coquelet, C.; Richon, D.; Naidoo, P.; Ramjugernath, D. Vapor-Liquid Equilibrium

Data for Binary Systems Consisting of Either Hexafluoropropene (HFP) or 2,2,3-Trifluoro-3-(trifluoromethyl)oxirane (HFPO) with Carbon Dioxide (R-744) or 2,2-Dichloro-1,1,1-trifluoroethane (R-123). *J. Chem. Eng. Data* **2011**, *56*, 74–78.

(6) Conradie, F. J.; Crouse, P. L.; Courtial, X.; van der Walt, I. J.; Ramjugernath, D. Isothermal Vapor-Liquid Equilibrium Data for the 1,1,2,2-Tetrafluoroethene + 1,1,2,2,3,3,3,4,4-Octafluorocyclobutane Binary System: Measurement and Modeling from (248 to 283) K. *J. Chem. Eng. Data* **2012**, *57*, 1978–1983.

(7) Larsen, B. L.; Rasmussen, P. A modified UNIFAC group-contribution model for the prediction of phase equilibria and heats of mixing. *Ind. Eng. Chem. Res.* **1987**, *62*, 2274–2286.

(8) Holderbaum, B.; Gmehling, J. PSRK: A group contribution Equation of State based on UNIFAC. *Fluid Phase Equilib.* **1991**, *70*, 251–265.

(9) Gmehling, J.; Li, J.; Schiller, M. A modified UNIFAC model. 2: Present parameter matrix and results for different thermodynamic properties. *Ind. Eng. Chem. Res.* **1992**, *32*, 178–193.

(10) Peng, D. Y.; Robinson, D. B. A new two parameter Equation of State. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59–64.

(11) Mathias, P. M.; Copeman, T. W. Extension of the Peng-Robinson Equation of State to complex mixtures: Evaluation of various forms of the local composition concept. *Fluid Phase Equilib.* **1983**, *13*, 91–108.

(12) Wong, D. S. H.; Sandler, S. I. A theoretically correct mixing rule for cubic equations of state. *AIChE J.* **1992**, *38*, 671–680.

(13) Renon, H.; Prausnitz, J. M. Local composition in thermodynamic excess function for liquid mixtures. *AIChE J.* **1968**, *14*, 135–144.

(14) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*; McGraw-Hill Book Company: New York, 1987.

(15) Daubert, T. E.; Danner, R. P.; Sibul, H. M.; Stebbins, C. C. *Physical and Thermodynamic Properties of Pure Chemicals*; Taylor & Francis: London, 1998.

(16) Guilbot, P.; Valtz, A.; Legendre, H.; Richon, D. On Line Sampler-Injector, a reliable tool for HT-HP Sampling and on line GC analysis. *Analysis* **2000**, *28*, 426–431.

(17) Taylor, B. N.; Mohr, P. J.; Douma, M. *The NIST Reference on constants, units, and uncertainty*; NIST: Gaithersburg, MD, 2007; available from: <http://www.physics.nist.gov/cuu/index.html>.

(18) Taylor, B. N.; Kuyatt, C. E. *Guidelines for evaluating and expressing the uncertainty of NIST measurement results*, technical report; National Institute of Standards and Technology: Gaithersburg, MD, 1994.

(19) Soo, C.-B. *Experimental Thermodynamic Measurements of Biofuel-related Associating Compounds and Modeling using the PC-SAFT Equation of State*. Ph.D. Thesis (Eng.), Mines de Paris, Paris, France, 2011.

(20) Nelson, W. M. *The Separation of Trichlorosilane: Measurement, Modeling and Simulation*. Ph.D. Thesis (Eng.), University of KwaZulu-Natal, Durban, South Africa, 2012.

(21) AspenTech. <http://aspentech.com>, 2010.

(22) Britt, H. I.; Luecke, R. H. The Estimation of Parameters in Nonlinear, Implicit Models. *Technometrics* **1973**, *15*, 233–238.

(23) Coquelet, C.; Ramjugernath, D.; Madani, H.; Naidoo, P.; Meniai, A. H. Experimental Measurement of Vapor Pressures and Densities of Pure Hexafluoropropylene. *J. Chem. Eng. Data* **2010**, *55*, 2093–2099.

(24) Yaws, C. L. *Yaws Handbook of Antoine Coefficients for Vapor Pressure*, 2nd electronic ed.; Knovel: Norwich, NY, 2009.