J. Chem. Eng. Data **1996,** *41,* 43−46

Vapor−Liquid Equilibria for Hydrogen Fluoride + Difluoromethane, + 1,1,1,2-Tetrafluoroethane, and + 1-Chloro-1,2,2,2-tetrafluoroethane at 283.3 and 298.2 K

Jongcheon Lee and Hwayong Kim*

Department of Chemical Engineering, Seoul National University, 56-1 Shinlimdong, Kwanak-ku,
Seoul 151-742, Korea

Jong Sung Lim, Jae-Duck Kim, and Youn Yong Lee

CFC Alternatives Technology Center, KIST, P.O. Box 131, Cheongryang, Seoul 130-650, Korea

Isothermal vapor−liquid equilibria for hydrogen fluoride (HF) + difluoromethane (HFC-32), HF + 1,1,1,2-tetrafluoroethane (HFC-134a), and HF + 1-chloro-1,2,2,2-tetrafluoroethane (HCFC-124) were measured by the *P*−*T*−*x* method at 283.3 and 298.2 K. Vapor compositions were calculated from these results. Among these systems, the HF + HFC-134a and HF + HCFC-124 systems exhibit minimum boiling azeotropes at both temperatures.

Introduction

Hydrogen fluoride is used in the HF alkylation process and in the manufacture of refrigerants and other halogenated compounds. The production of refrigerants involves the separation of multicomponent mixtures containing hydrogen fluoride, hydrogen chloride, and various chlorinated and fluorinated hydrocarbons. Therefore, it is essential to know the phase behavior of these mixtures. Because of the toxic and corrosive nature of HF, very few measurements on HF-containing systems are available in the literature.

In this work, we measured the vapor−liquid equilibria by the total pressure−temperature−liquid composition (*P*−*T*−*x*) method. The *P*−*T*−*x* method has the advantage that no vapor or liquid samples are taken. This is an advantage for systems which are difficult to analyze, such as HF-containing systems.

Experimental Section

Chemicals. The purities of the chemicals were guaranteed by the manufacturers as shown in Table 1. They were used without any further purification.

Experimental Apparatus. An apparatus similar to that used by Gillespie et al. (1985a) was used. The apparatus was placed in a steel housing for safety. The cell was made of 304 stainless steel and had an internal volume of 300 cm^3. During the run, the cell was submerged in a constant temperature bath kept constant by a Haake circulator, model F3. The bath temperature was constant to ±0.02 K.

The temperatures were measured by a standard platinum resistance thermometer, with an uncertainty in the temperature measurement estimated to be ±0.02 K. The total pressure was measured by a SENSOTEC digital pressure transducer, model TJE-AP122-DTS. It was specially constructed to withstand corrosive HF and was calibrated by SENSOTEC. The uncertainty of the pressure measurement is estimated to be within ±0.01 bar.

Experimental Procedure. After the whole system had been evacuated by a vacuum pump, a known mass of HF was introduced into the cell from a charging cylinder. The contents of the cell were allowed to equilibrate, and the pressure was measured. Known increments of the refrigerant were then charged into the cell. After each increment, the contents were agitated manually to achieve equilibration before the pressure was measured. The mass of the charge in the cell was measured by the mass change of the charging cylinder. The total volume of the liquid was always at least 60% of the cell volume.

Because the dead volume in the connecting line between the cylinder valve and cell valve is approximately 0.5 cm^3, material loss was negligible. Before each charging step, the materials in the dead volume were removed by a vacuum pump.

Table 1. Origin and Purity of the Chemicals

component	origin	purity/ (wt %)
HF	ULSAN Chemical Co., Korea	>99.9
HFC-32	Korea Institute of Science & Technology	>99.9
HFC-134a	DAIKIN Industries, Ltd.	>99.9
HCFC-124	DuPont	>99.9

Table 2. Characteristic Properties of the Chemicals

component	T_c/K	P_c/bar	ω	source
HF	461.0	64.8	0.329	Reid et al. (1987)
HFC-32	351.6	58.3	0.271	Lee and Chao (1991)
HFC-134a	374.3	40.7	0.327	Lee and Chao (1991)
HCFC-124	395.7	36.3	0.286	Lee and Chao (1991)

Table 3. Comparison of the Measured and Literature Vapor Pressures

		P/bar		
component	*T*/K	measd	lit.	source
HF	283.50	0.71	0.708	*a*
	298.50	1.21	1.215	*a*
HFC-32	283.32	11.19	11.129	*b*
	298.15	17.01	16.90	*b*
HFC-134a	283.27	4.17	4.167	*b*
	298.15	6.66	6.66	*b*
HCFC-124	283.45	2.37	2.369	*c*
	298.20	3.87	3.835	*c*

[a] Data table from Simons (1924). [b] Antoine equation from Sato et al. (1994). [c] Antoine equation from Shankland et al. (1990).

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* To whom correspondence should be addressed.

0021-9568/96/1741-0043$12.00/0

Table 4. Modified Wilson Equation Parameters and AAD (%) of *P*

system	T/K	modified Wilson equation parameters	δP^a/%
HF + HFC-32	283.32	$a = 0.1356$, $b = 0.3039$, $c = 0.8742$	0.13
	298.15	$a = 0.1537$, $b = 0.2938$, $c = 0.8408$	0.13
HF + HFC-134a	283.27	$a = 0.0897$, $b = 0.1904$, $c = 0.9937$	0.68
	298.15	$a = 0.0828$, $b = 0.1588$, $c = 0.9368$	0.36
HF + HCFC-124	283.45	$a = 0.0536$, $b = 0.0999$, $c = 1.0195$	0.66
	298.20	$a = 0.0746$, $b = 0.1118$, $c = 1.0235$	0.42

^{a} $\delta P = (1/N)\sum_i^N |(P_{\text{exptl},i} - P_{\text{calcd},i})/P_{\text{exptl},i}| \times 100$.

Table 5. Vapor−Liquid Equilibrium Measurements for the HF (1) + HFC-32 (2) System

x_1	y_1 (calcd)	P/bar exptl	P/bar calcd	γ_1	γ_2
		$T = 283.32$ K			
1.0000	1.0000	0.71	0.71	1.0000	6.0308
0.9444	0.4270	3.28	3.28	1.0069	4.7169
0.8851	0.2660	5.08	5.08	1.0274	3.7925
0.7629	0.1518	7.24	7.21	1.1069	2.6657
0.7426	0.1417	7.41	7.44	1.1249	2.5376
0.5925	0.0952	8.67	8.67	1.3099	1.8670
0.4909	0.0766	9.21	9.19	1.5058	1.5836
0.4825	0.0752	9.20	9.22	1.5256	1.5641
0.4500	0.0704	9.38	9.36	1.6088	1.4932
0.3757	0.0603	9.63	9.63	1.8484	1.3545
0.3029	0.0512	9.86	9.88	2.1813	1.2444
0.2597	0.0458	10.00	10.02	2.4511	1.1889
0.2159	0.0403	10.19	10.17	2.8104	1.1393
0.1619	0.0332	10.38	10.36	3.4434	1.0869
0.1421	0.0304	10.44	10.43	3.7565	1.0701
0.1308	0.0287	10.48	10.48	3.9626	1.0611
0.0724	0.0194	10.73	10.74	5.5305	1.0224
0.0566	0.0164	10.82	10.83	6.1874	1.0145
0.0522	0.0156	10.85	10.85	6.3979	1.0126
0.0447	0.0139	10.89	10.89	6.7903	1.0095
0.0000	0.0000	11.19	11.19	10.5405	1.0000
		$T = 298.15$ K			
1.0000	1.0000	1.21	1.21	1.0000	5.7055
0.9582	0.5340	4.03	4.02	1.0040	4.7260
0.9171	0.3672	6.05	6.07	1.0147	4.0253
0.8626	0.2612	8.10	8.06	1.0379	3.3501
0.7784	0.1819	10.09	10.14	1.0923	2.6486
0.6255	0.1176	12.39	12.37	1.2531	1.9128
0.4736	0.0845	13.76	13.71	1.5267	1.5034
0.3815	0.0697	14.29	14.31	1.7892	1.3357
0.3424	0.0640	14.53	14.55	1.9368	1.2770
0.3142	0.0600	14.71	14.72	2.0620	1.2385
0.2423	0.0501	15.16	15.15	2.4819	1.1534
0.2018	0.0444	15.40	15.40	2.8131	1.1130
0.1653	0.0391	15.63	15.63	3.2040	1.0809
0.1390	0.0351	15.80	15.81	3.5643	1.0605
0.1131	0.0309	15.98	15.99	4.0108	1.0426
0.0647	0.0216	16.35	16.38	5.2390	1.0161
0.0441	0.0165	16.56	16.57	6.0183	1.0080
0.0307	0.0126	16.70	16.70	6.6571	1.0041
0.0267	0.0112	16.74	16.74	6.8736	1.0032
0.0000	0.0000	17.01	17.01	8.7441	1.0000

Table 6. Vapor−Liquid Equilibrium Measurements for the HF (1) + HFC-134a (2) System

x_1	y_1 (calcd)	P/bar exptl	P/bar calcd	γ_1	γ_2
		$T = 283.27$ K			
1.0000	1.0000	0.70	0.71	1.0000	12.8423
0.9783	0.7119	1.63	1.59	1.0021	10.6072
0.9761	0.6934	1.63	1.66	1.0025	10.4180
0.9558	0.5680	2.14	2.22	1.0080	8.9155
0.9293	0.4732	2.86	2.76	1.0190	7.4518
0.8397	0.3383	3.66	3.65	1.0819	4.6658
0.7961	0.3086	3.83	3.85	1.1250	3.9132
0.7081	0.2723	4.06	4.08	1.2373	2.9278
0.6479	0.2566	4.15	4.16	1.3365	2.4883
0.5598	0.2400	4.23	4.23	1.5249	2.0347
0.5569	0.2395	4.24	4.23	1.5322	2.0225
0.5245	0.2345	4.24	4.25	1.6192	1.8952
0.3667	0.2130	4.32	4.30	2.2629	1.4499
0.2982	0.2022	4.33	4.32	2.7462	1.3170
0.2295	0.1875	4.32	4.32	3.4971	1.2081
0.2006	0.1789	4.31	4.33	3.9501	1.1685
0.1217	0.1405	4.35	4.33	6.0681	1.0774
0.0920	0.1163	4.31	4.32	7.5522	1.0496
0.0664	0.0899	4.31	4.31	9.5047	1.0292
0.0614	0.0842	4.30	4.30	9.9998	1.0256
0.0348	0.0527	4.28	4.28	13.6870	1.0097
0.0255	0.0415	4.28	4.26	15.6180	1.0055
0.0000	0.0000	4.17	4.17	24.5471	1.0000
		$T = 298.15$ K			
1.0000	1.0000	1.21	1.21	1.0000	13.2374
0.9783	0.7153	2.63	2.60	1.0023	10.6594
0.9338	0.4995	4.18	4.25	1.0184	7.4839
0.8715	0.3887	5.36	5.38	1.0588	5.1891
0.8068	0.3345	5.96	5.95	1.1179	3.9002
0.7407	0.3013	6.31	6.28	1.1954	3.0988
0.6543	0.2721	6.57	6.53	1.3260	2.4377
0.6019	0.2583	6.66	6.63	1.4252	2.1578
0.4168	0.2180	6.85	6.84	1.9755	1.5379
0.3476	0.2030	6.90	6.89	2.3244	1.3909
0.2856	0.1881	6.93	6.92	2.7690	1.2828
0.2469	0.1773	6.95	6.94	3.1484	1.2245
0.2009	0.1622	6.93	6.95	3.7654	1.1630
0.1205	0.1248	6.95	6.96	5.7363	1.0744
0.1169	0.1227	6.94	6.96	5.8735	1.0709
0.0964	0.1092	6.93	6.95	6.7961	1.0525
0.0862	0.1018	6.93	6.95	7.3688	1.0440
0.0834	0.0997	6.96	6.95	7.5428	1.0417
0.0348	0.0562	6.85	6.88	12.5929	1.0097
0.0255	0.0456	6.84	6.85	14.3608	1.0056
0.0000	0.0000	6.66	6.66	22.6897	1.0000

The liquid composition was determined from the known masses of each component added to the cell without applying any correction. The uncertainty in the liquid composition measurements is estimated to be ±0.05 mol %. The vapor composition is calculated using Schotte's method (1980).

Results and Discussion

At low to moderate pressures, the Poynting factor is negligible, so the equilibrium relations are as follows:

$$z_i \phi_i P = x_i \gamma_i \phi_i^0 P_i^0 \tag{1}$$

where z_i is the mole fraction of component i in the vapor phase, ϕ_i is the fugacity coefficient of component i in the vapor phase, P is the total pressure, x_i is the mole fraction of component i in the liquid phase, γ_i is the activity coefficient of component i in the liquid phase, ϕ_i^0 is the pure component fugacity coefficient at saturation, and P_i^0 is the vapor pressure of pure component i.

HF shows strong association in the vapor phase, which must be considered in the calculations. There have been conflicting models proposed for the description of the self-association of HF in the vapor phase. We used the monomer−dimer−hexamer−octamer model proposed by Schotte (1980) to allow for the vapor phase association. Tamir et al. (1978) have shown for a mixture of monomers, dimers, etc. that the fugacity coefficients of all of these species are equal. Then the true mole fractions in pure HF in the gas phase can be expressed through the equilibrium constants of various reactions:

$$z_{12}^0 = K_2((f_{11}^0)^2/\phi_1^0 P_1^0) \tag{2.1}$$

$$z_{16}^0 = K_6((f_{11}^0)^6/\phi_1^0 P_1^0) \tag{2.2}$$

$$z_{18}^0 = K_s((f_{11}^0)^8/\phi_1^0 P_1^0) \tag{2.3}$$

Table 7. Vapor–Liquid Equilibrium Measurements for the HF (1) + HCFC-124 (2) System

x_1	y_1 (calcd)	P/bar exptl	P/bar calcd	γ_1	γ_2
		T = 283.45 K			
1.0000	1.0000	0.71	0.71	1.0000	27.4773
0.9769	0.6913	1.66	1.68	1.0043	18.6443
0.9432	0.5552	2.33	2.31	1.0215	12.2898
0.8933	0.4851	2.69	2.65	1.0614	7.9388
0.8732	0.4708	2.75	2.72	1.0810	6.9101
0.8100	0.4448	2.83	2.82	1.1541	4.8644
0.7323	0.4304	2.86	2.87	1.2680	3.5342
0.7092	0.4279	2.87	2.87	1.3076	3.2647
0.6134	0.4217	2.88	2.89	1.5065	2.4732
0.5922	0.4209	2.89	2.89	1.5597	2.3463
0.5155	0.4194	2.88	2.89	1.7901	1.9773
0.2339	0.4156	2.89	2.89	3.9342	1.2519
0.1046	0.3689	2.79	2.84	8.4707	1.0780
0.0821	0.3376	2.79	2.81	10.4954	1.0546
0.0792	0.3322	2.77	2.80	10.8247	1.0517
0.0629	0.2934	2.75	2.77	13.1078	1.0365
0.0559	0.2713	2.76	2.75	14.3881	1.0304
0.0269	0.1404	2.65	2.62	23.5258	1.0092
0.0184	0.0979	2.60	2.57	28.5068	1.0048
0.0155	0.0844	2.58	2.55	30.6607	1.0035
0.0000	0.0000	2.37	2.37	49.4479	1.0000
		T = 298.20 K			
1.0000	1.0000	1.21	1.21	1.0000	24.2807
0.9739	0.6870	2.77	2.78	1.0050	16.4294
0.9020	0.4961	4.25	4.22	1.0504	8.1378
0.8762	0.4732	4.42	4.39	1.0739	6.8081
0.8226	0.4455	4.61	4.59	1.1325	5.0370
0.7758	0.4321	4.68	4.66	1.1937	4.0812
0.6994	0.4201	4.69	4.71	1.3160	3.0984
0.6127	0.4134	4.71	4.73	1.4964	2.4231
0.5127	0.4099	4.75	4.74	1.7843	1.9316
0.4367	0.4085	4.73	4.74	2.0928	1.6725
0.3975	0.4078	4.75	4.74	2.2979	1.5643
0.2799	0.4024	4.71	4.74	3.2501	1.3114
0.2220	0.3942	4.69	4.73	4.0713	1.2164
0.1279	0.3487	4.64	4.66	6.7968	1.0934
0.0881	0.2936	4.57	4.58	9.3322	1.0526
0.0786	0.2736	4.55	4.55	10.2183	1.0439
0.0153	0.0738	4.19	4.15	24.8185	1.0026
0.0105	0.0556	4.11	4.08	27.4687	1.0013
0.0000	0.0000	3.87	3.87	35.3636	1.0000

where z^0_{12}, z^0_{16}, and z^0_{18} are the true mole fractions of dimers, hexamers, and octamers in pure HF vapor, K_2, K_6, and K_8 are the equilibrium constants of the dimer, hexamer, and octamer, and $f^0_{11} = z^0_{11}\phi^0_1 P^0_1$ is the fugacity of HF monomer in pure HF.

The equilibrium constants are given by Schotte (1980):

$$K_2 = \exp[(6429.7/(T/\mathrm{K}) - 24.16)] \tag{3.1}$$

$$K_6 = \exp[(21102.0/(T/\mathrm{K}) - 69.80)] \tag{3.2}$$

$$K_8 = \exp[(25225.7/(T/\mathrm{K}) - 83.57)] \tag{3.3}$$

where $K_n = (\mathrm{bar})^{-(n-1)}$. Then for pure HF

$$\phi^0_1 P^0_1 = f^0_{11} + K_2(f^0_{11})^2 + K_6(f^0_{11})^6 + K_8(f^0_{11})^8 \tag{4}$$

Equation 4 can be solved to give f^0_{11} with ϕ^0_1 and the experimental vapor pressure P^0_1. The pure component fugacity coefficient, ϕ^0_i is calculated by the Peng–Robinson (1976) equation of state. Critical properties and acentric factors used to calculate the parameters for the Peng–Robinson equation of state are given in Table 2.

For HF in the vapor mixture

$$\phi_1 P_1 = f_{11} + K_2 f_{11}{}^2 + K_6 f_{11}{}^6 + K_8 f_{11}{}^8 \tag{5.1}$$

$$f_{11} = \gamma_1 x_1 f^0_{11} \tag{5.2}$$

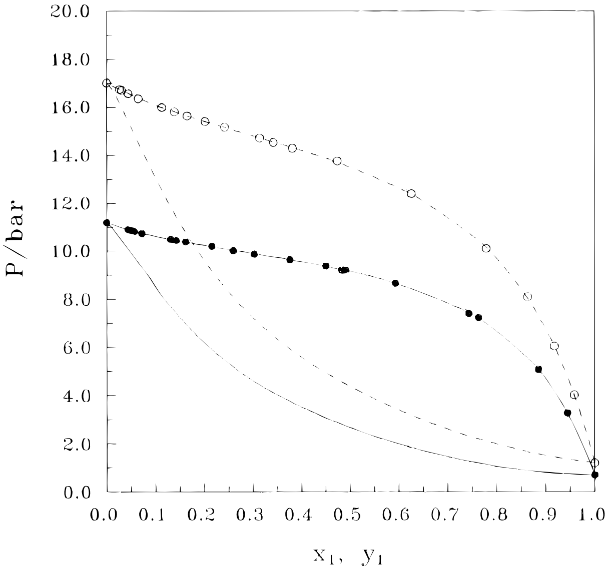

Figure 1. P–x diagram for the HF (1) + HFC-32 (2) system at 283.32 and 298.15 K: ●, experimental at 283.32 K; ○, experimental at 298.15 K; —, calculated at 283.32 K; - - -, calculated at 298.15 K.

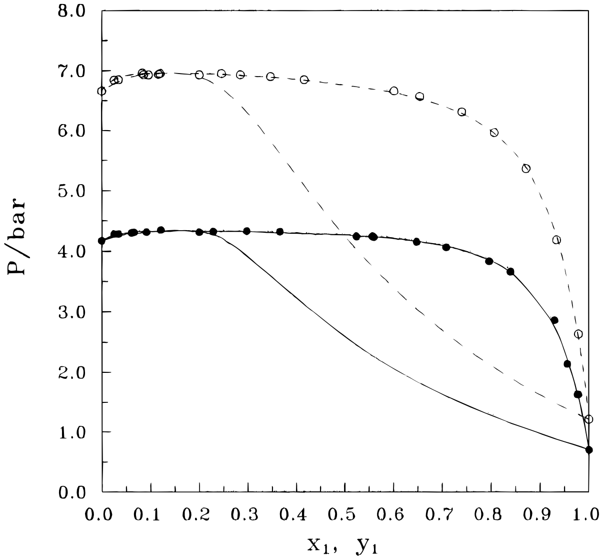

Figure 2. P–x diagram for the HF (1) + HFC-134a (2) system at 283.27 and 298.15 K: ●, experimental at 283.27 K; ○, experimental at 298.15 K; —, calculated at 283.27 K; - - -, calculated at 298.15 K.

where P_1 is the partial pressure of total HF in the vapor mixture and f_{11} is the fugacity of HF monomer in the mixture. Equation 5 can be solved to give P_1 with ϕ_1 and γ_i. We used the Peng–Robinson equation of state to calculate the fugacity coefficient ϕ_i with true vapor compositions, $z_1 = \sum z_{1i}$ and z_2. For mixtures we used the van der Waals one-fluid mixing rule without the binary interaction parameter. The liquid phase activity coefficient can be calculated by the modified Wilson (1985b) equation. The total pressure is $P = P_1 + P_2$, where P_2 is calculated from eq 1 for a nonassociating component.

For the BUBL P calculation, we calculated the total pressure P and the true vapor composition z_i with known x_i and T. The apparent vapor composition was calculated by using eq 7.

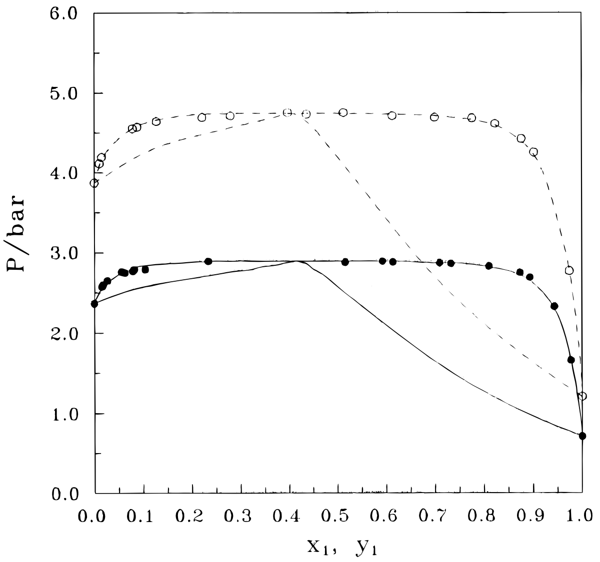

Figure 3. $P-x$ diagram for the HF (1) + HCFC-124 (2) system at 283.45 and 298.20 K: ●, experimental at 283.45 K; ○, experimental at 298.20 K; —, calculated at 283.45 K; - - -, calculated at 298.20 K.

The apparent vapor composition on the basis of a molecular weight of 20.006 for HF is

$$y_1 = \frac{z_{11} + 2z_{12} + 6z_{16} + 8z_{18}}{z_{11} + 2z_{12} + 6z_{16} + 8z_{18} + z_2} \tag{6}$$

where z_{11}, z_{12}, z_{16}, and z_{18} are the true mole fractions of the monomer, dimer, hexamer, and octamer in the vapor mixture, respectively. Since $z_{11} = f_{11}/\phi_1 P$, $z_{12} = K_2 (f_{11}^2/\phi_1 P)$, $z_{16} = K_6(f_{11}^6/\phi_1 P)$, $z_{18} = K_8(f_{11}^8/\phi_1 P)$, and $z_2 = P_2/P$

$$y_1 = \frac{S}{S + \phi_1 P_2} \tag{7}$$

where $S = f_{11} + 2K_2 f_{11}^2 + 6K_6 f_{11}^6 + 8K_8 f_{11}^8$.

The modified Wilson equation is

$$\ln \gamma_1 = c\left[-\ln(x_1 + ax_2) - \frac{x_1}{x_1 + ax_2} - \frac{bx_2}{x_2 + bx_1} + 1\right] \tag{8}$$

$$\ln \gamma_2 = c\left[-\ln(x_2 + bx_1) - \frac{ax_1}{x_1 + ax_2} - \frac{x_2}{x_2 + bx_1} + 1\right] \tag{9}$$

where a, b, and c are parameters.

The Marquardt algorithm (1973) was applied to obtain the modified Wilson equation parameters with the following objective function:

$$\text{obj} = \sum_j \left[\left(\frac{P_{j,\text{exptl}} - P_{j,\text{calcd}}}{P_{j,\text{exptl}}}\right) \times 100\right]^2 \tag{10}$$

Table 3 is a comparison of measured and literature pure component vapor pressures. The average absolute deviation between measured and literature values is 0.36%. Both modified Wilson equation parameters and the average absolute deviation between measured and calculated pressures are listed in Table 4.

The experimental $P-T-x$ data are summarized in Tables 5−7. Each table lists the mole fraction of the liquid and vapor phases in equilibrium, the measured and calculated pressures, and the activity coefficient of each component.

The results of $P-x$ measurements on HF + HFC-32 at 283.32 and 298.15 K are listed in Table 5. The $P-x$ results at 283.32 and 298.15 K are shown in Figure 1. Both isotherms exhibit no azeotrope.

The results for HF + HFC-134a are listed in Table 6. The $P-x$ values at 283.27 and 298.15 K are shown in Figure 2. This system exhibits a minimum boiling azeotrope.

HF + HCFC-124 was studied at 283.45 and 298.20 K. The results of these measurements are found in Table 7. Figure 3 shows the $P-x$ data. The system exhibits a minimum boiling azeotrope.

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Received for review April 21, 1995. Revised July 29, 1995. Accepted September 27, 1995.[⊗]

JE9500946

[⊗] Abstract published in *Advance ACS Abstracts*, November 1, 1995.