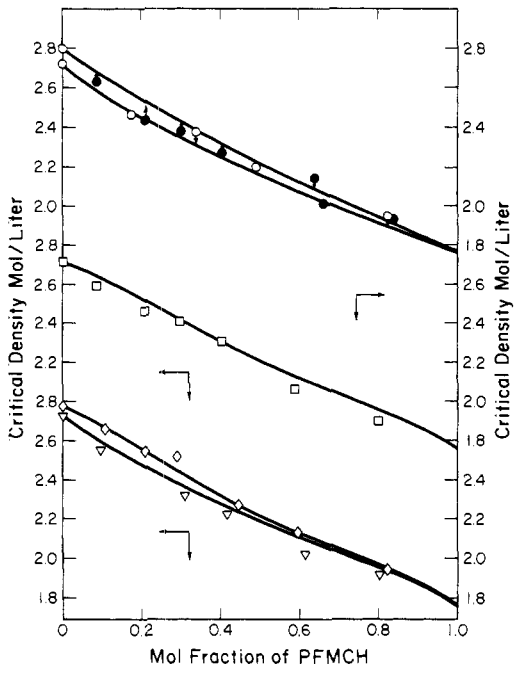

Figure 4. Critical density–composition relations of binary systems of PFMCH with isomeric hexanes. Predicted values: (—). Experimental points: (●) 2,2-dimethylbutane; (○) *n*-hexane; (◇) 2-methylpentane; (▽) 2,3-dimethylbutane; (□) 3-methylpentane. $\xi = 0.885$ for all systems.

ρ	density
ξ	interaction coefficient

Subscripts

1, 2	component 1, 2
c	critical
cm	pseudocritical value for mixture
i, *j*	component *i*, *j*
vap	vaporization
x, *v*	differentiation with respect to *x*, *v*

Superscripts

G	gas
L	liquid

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Study of the Critical and Azeotropic Behavior of Binary Mixtures. 2. *PVT–x* Data and Azeotropic States of Perfluoromethylcyclohexane–Isomeric Hexane Systems

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***PVT–x* data for five binary systems composed of the isomers of hexane with perfluoromethylcyclohexane as the common component are reported in this paper. All of these systems form positive azeotropes which persist in their critical regions. The locus of azeotropic points for each system and its prediction using an extended corresponding states principle is also reported.**

Introduction

An investigation of the *PVT–x* relations of a series of binary systems composed of the isomers of hexane with perfluoromethylcyclohexane (PFMCH) as a common component was undertaken to obtain information on the relative effect of molecular structure on the phase diagrams of such mixtures. These systems were found to form positive azeotropes which persist up to the critical locus curve. The critical loci of PFMCH–isomeric hexane mixtures and their correlation and prediction using an extended corresponding states principle were reported in part 1 of this paper (*1*). It was found that the critical loci of all these systems exhibit a minimum temperature point which is characteristic of systems which form positive azeotropes in their critical region. It was further shown that the critical loci of PFMCH–isomeric hexane systems could be predicted by the extended corresponding states approach, using only a single adjustable binary interaction coefficient obtained from the correlation of the critical states of PFMCH–*n*-hexane mixtures.

In this paper, we report the measurements of dew and bubble points as well as azeotropic states of PFMCH–isomeric hexane systems. The predictive capabilities of the extended corre-

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Table I. Perfluoromethylcyclohexane (1)-*n*-Hexane (2) Data

	dew point		bubble point	
temp, K	press., bar	vol, cm^3 mol^{-1}	press., bar	vol, cm^3 mol^{-1}
		$x_1 = 0.8171$		
478.16	21.364	620.26	21.554	499.65
474.11	19.620	908.21	20.507	376.01
468.12	17.693	1137.41	18.774	337.41
463.04	16.145	1339.56	17.384	317.64
453.13	13.540	1755.18	14.823	295.80
443.02	11.240	2239.46	12.543	280.52
433.08	9.201	2849.55	10.577	266.65
423.00	7.587	3605.39	8.881	257.08
403.07	4.912	5727.12	6.154	240.47
383.07	3.092	9232.89	4.126	228.27
		$x_1 = 0.6603$		
473.67	21.971	605.06	22.148	436.61
469.12	20.178	866.66	20.690	351.94
464.10	18.510	1051.94	19.163	321.57
453.07	15.256	1471.77	16.050	289.17
443.02	12.764	1889.74	13.619	275.51
423.00	8.751	2979.20	9.560	250.00
403.12	5.688	4841.68	6.459	231.31
383.07	3.432	8141.80	4.257	212.33
		$x_1 = 0.4860$		
473.51	23.288	525.85	23.310	502.79
469.10	21.607	785.49	21.743	330.03
463.05	19.631	986.53	19.768	303.60
453.09	16.550	1326.67	16.778	276.23
443.02	13.862	1681.91	14.119	254.61
422.99	9.588	2641.88	9.875	233.79
403.07	6.318	4330.21	6.700	216.44
383.02	4.128	6804.37	4.347	210.46
		$x_1 = 0.3342$		
478.25	24.769	525.35	24.873	417.15
473.10	22.741	760.95	22.946	308.65
468.10	20.956	918.54	21.170	285.22
463.04	19.327	1069.16	19.545	269.76
453.09	16.401	1388.47	16.694	248.20
443.02	13.780	1758.52	14.027	235.97
422.99	9.597	2711.47	9.837	216.60
403.13	6.419	4199.17	6.622	203.86
383.09	4.123	6435.61	4.331	189.19
		$x_1 = 0.1731$		
489.75	27.258	529.35	27.517	382.30
484.12	24.833	742.92	25.518	289.24
478.11	22.540	915.14	23.417	264.54
473.10	20.795	1055.22	21.745	253.06
463.04	17.621	1351.93	18.651	232.88
452.99	14.931	1693.39	15.888	219.85
443.03	12.556	2086.00	13.497	212.29
423.00	8.675	2952.99	9.475	195.01
403.07	5.600	5064.97	6.456	182.24
383.19	3.547	7949.79	4.255	174.56
		$x_1 = 0.000$		
507.50	30.336	423.84	30.268	330.29
503.21	28.478	627.46	28.564	281.14
493.11	24.501	880.92	24.619	241.74
483.11	21.159	1116.86	21.209	223.58
473.10	18.084	1410.35	18.256	210.15
463.04	15.348	1712.72	15.468	199.35
453.08	12.890	2106.99	13.030	190.50
443.02	10.833	2544.73	10.951	182.22
422.99	7.437	3849.80	7.544	170.73
403.07	4.963	5643.05	4.969	162.60
383.19	3.137	7867.47	3.161	155.87

sponding states method are tested further, and the method is used for the calculation of azeotropic loci of binary systems of PFMCH with the isomeric hexanes.

Experimental Section

The experimental details have been reported fully in part 1 and are not repeated here.

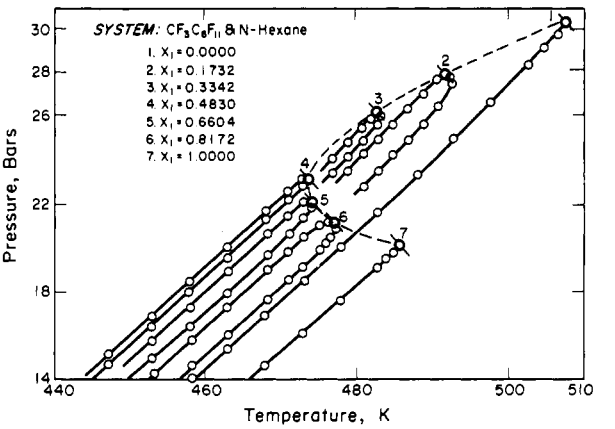

Figure 1. Pressure–temperature phase diagram for the PFMCH–*n*-hexane system: (⊗) critical points of mixtures.

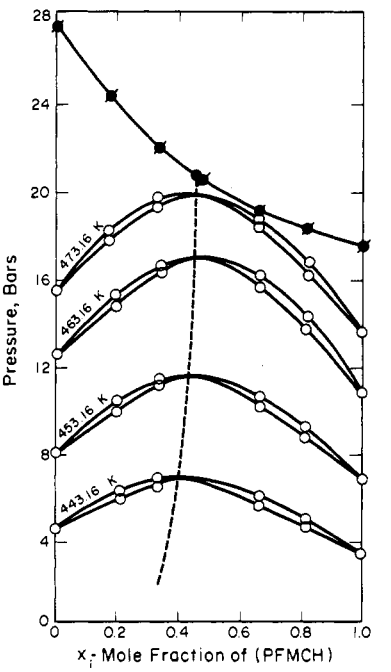

Figure 2. Pressure–composition diagram for the PFMCH–*n*-hexane system: (---) locus of azeotropes; (●) calculated critical locus curve of system.

Results

Results in the Vapor–Liquid Region for the Binary System. The pressure, temperature, and specific volume data for the vapor–liquid region for the five binary systems are presented in Tables I–V. The data cover a range from 383.16 K and a pressure of approximately ~3.45 bar to the highest temperature and pressure at which liquid and vapor coexist. Only selected data points are presented in Tables I–V. Detailed results can be found in ref *2*.

Rather than present several repetitious PVT–x_1 diagrams for each of the five binary systems, we chose the perfluoromethylcyclohexane–*n*-hexane system as a representative sample, and data from Table I were employed to construct PT, P–x_1 and TV diagrams; these diagrams are presented as Figures 1, 2, and 3, respectively.

Azeotropic States. At a given temperature, the azeotropic pressure and composition were determined by using the Gibbs–Konowalow theorem. The theorem states (*4*), "If in a series of isothermal equilibrium states of a two phase binary system, the composition of the two phases becomes the same, then the pressure must pass through an extreme value." Thus,

Table II. Perfluoromethylcyclohexane-3-Methylpentane Data

	dew point		bubble point	
temp, K	press., bar	vol, cm^3 mol^{-1}	press., bar	vol, cm^3 mol^{-1}
		$x_1 = 0.7951$		
476.66	21.319	685.16	21.734	427.60
473.10	19.903	879.89	20.708	368.09
463.04	16.618	1271.67	17.827	317.40
453.09	13.869	1676.19	15.112	291.98
443.02	11.461	2160.88	12.837	275.54
422.99	7.641	3561.71	9.060	251.70
403.07	4.988	5572.22	6.191	236.31
383.06	3.141	8841.47	4.118	223.97
		$x_1 = 0.5869$		
472.67	22.996	564.78	23.166	428.72
468.10	21.130	803.44	21.569	337.92
463.04	19.372	1006.21	20.101	310.47
453.09	16.299	1346.46	17.086	281.74
443.02	13.600	1745.58	14.453	262.72
422.99	9.116	2899.56	10.199	238.39
403.07	6.136	4477.32	7.013	222.96
383.06	3.858	7164.52	4.687	209.53
		$x_1 = 0.4045$		
474.06	24.502	559.29	24.641	370.73
468.10	22.192	804.52	22.513	301.97
462.57	20.239	979.25	20.657	279.90
453.09	17.327	1269.48	17.724	257.93
443.02	14.611	1615.28	15.053	241.47
423.00	10.149	2516.07	10.633	220.23
403.07	6.846	3950.64	7.314	205.96
383.06	4.435	6151.45	4.918	190.61
		$x_1 = 0.2952$		
478.44	25.709	520.32	25.833	365.10
474.10	23.946	710.03	24.261	300.99
468.10	21.754	889.19	22.132	271.47
463.04	20.121	1026.81	20.529	257.29
453.09	17.057	1325.52	17.462	238.60
443.02	14.405	1662.30	14.791	225.36
422.99	10.021	2594.03	10.419	207.00
403.07	6.792	3934.01	7.165	192.98
383.06	4.404	6185.02	4.722	182.12
		$x_1 = 0.2062$		
484.11	27.132	529.08	27.411	358.26
478.10	24.592	753.10	25.210	283.15
473.14	22.704	889.07	23.441	262.10
463.04	19.297	1173.52	20.140	239.29
453.09	16.374	1470.90	17.172	224.38
443.07	13.794	1833.90	14.584	213.68
422.99	9.602	2821.54	10.304	195.55
403.07	6.474	4134.31	7.111	184.62
383.06	4.163	6453.76	4.698	172.37
		$x_1 = 0.0855$		
494.91	29.353	489.24	29.409	319.56
489.11	26.790	687.31	27.376	267.30
483.11	24.399	844.21	25.089	245.87
473.10	20.932	1087.75	21.685	224.91
463.04	17.808	1371.02	18.635	211.19
443.02	12.777	2066.43	13.513	192.73
422.93	8.887	3148.33	9.589	181.42
403.07	5.998	4592.39	6.545	171.13
383.06	3.792	7466.38	4.357	162.33

If the bubble and dew point pressures are plotted against composition at a given temperature and smooth curves are drawn through the data, both curves will exhibit a maximum, for positive azeotropy, at the azeotropic composition.

The method was applied to each system at temperatures from 398.16 K to the critical region by using increments of 5 K. When smooth values of the bubble and dew point data were plotted, as indicated above, two well-defined curves were obtained. For each temperature, the maxima on these curves could reliably be established. It was also observed that both maxima occurred at approximately the same composition. An average of the two values was taken as the experimental azeotropic pressure and

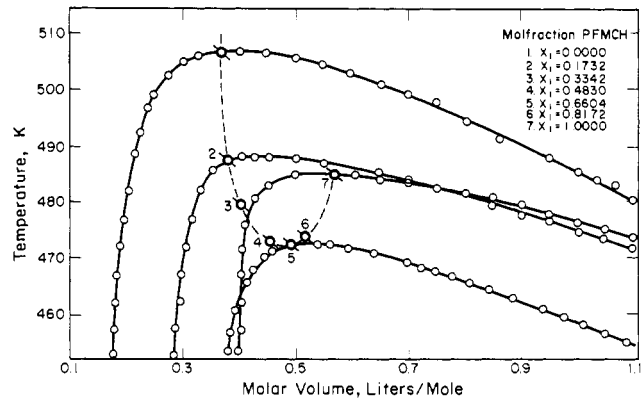

Figure 3. Temperature–volume diagram for PFMCH–*n*-hexane system.

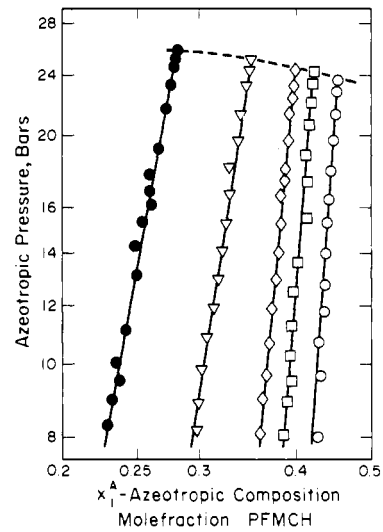

Figure 4. Composite log P^A vs. log x_1^A diagram of the PFMCH–isomeric hexane systems: (---) critical locus curve; (O)*n*-hexane; (□) 3-methylpentane; (◇) 2-methylpentane; (▽) 2,3-dimethylbutane; (●) 2,2-dimethylbutane.

composition. The results of these equations are presented in Table VI.

Correlation of the Data

Pressure–Temperature Correlation. A correlation described by Prigogine (*4*) was applied to the data in Table VI. Prigogine showed that the azeotropic pressure (P^A) can be related to the temperature (T) by the standard vapor pressure equation

$$\log (P^A) = A + B/T \qquad (1)$$

where P^A is in bars, T is in K, and A and B are constants. Equation 1 shows that the log of the azeotropic pressure is linear in $1/T$. The constants A and B were determined by a least-squares fit to the data and are presented in Table VII.

Pressure–Composition Correlation. The relationship between the azeotropic composition and the pressure is expressed satisfactorily by the equation of Othmer and Ten Eyck (*3*)

$$\log (P^A) = a + b(\log x_1^A) \qquad (2)$$

where x_1 is the mole fraction of PFMCH and P^A the azeotropic pressure. The least-squares constants a and b for each system are listed in Table VIII.

The azeotropic composition x_1 changes very little with pressure. This results from the fact that the temperature coefficients of the vapor pressure (dP/dT) for PFMCH and the hexanes are approximately the same. It is only when these coefficients are quite different from each other that the composition changes rapidly with the pressure.

Table III. Perfluoromethylcyclohexane-2-Methylpentane Data

	dew point		bubble point	
temp, K	press., bar	vol, cm³ mol⁻¹	press., bar	vol, cm³ mol⁻¹
	x_1 = 0.7980			
475.10	20.853	753.88	21.463	413.45
468.10	18.286	1072.04	19.372	344.43
463.04	16.700	1275.39	17.950	322.92
453.09	13.855	1699.48	15.341	293.43
443.02	11.394	2212.02	13.048	277.07
423.00	7.632	3609.93	9.192	252.90
403.11	5.039	5596.76	6.331	237.09
383.06	3.107	9063.53	4.204	223.82
	x_1 = 0.6087			
471.07	22.597	577.14	22.734	457.43
468.10	21.315	777.89	21.786	361.95
463.04	19.495	980.57	20.143	325.39
453.09	16.382	1339.65	17.206	291.34
443.02	13.581	1764.92	14.573	271.07
422.99	9.105	2918.49	10.297	243.49
403.07	6.105	4548.69	7.023	227.20
383.06	3.773	7477.78	4.615	210.45
	x_1 = 0.4104			
470.78	24.094	527.71	24.238	386.81
463.04	21.146	862.59	21.627	298.11
453.09	17.899	1171.42	18.484	266.33
443.02	15.046	1520.48	15.700	247.36
423.00	10.370	2395.29	11.155	222.39
403.07	6.918	3856.50	7.701	208.89
382.98	4.466	6061.19	5.167	192.28
	x_1 = 0.3077			
473.73	25.076	532.55	25.208	374.58
469.10	23.237	739.44	23.519	305.35
463.04	21.055	923.11	21.419	276.47
453.09	17.882	1218.06	18.280	252.61
442.98	15.061	1550.50	15.513	236.62
423.00	10.499	2341.76	10.968	213.36
403.07	7.110	3776.26	7.511	199.81
383.06	4.535	5976.62	4.970	186.68
	x_1 = 0.2059			
478.67	26.243	547.67	26.392	357.79
474.10	24.310	720.73	24.670	291.92
468.10	22.099	882.65	22.500	264.99
463.04	20.346	1022.87	20.803	251.61
453.09	17.310	1316.63	17.744	233.41
443.02	14.600	1649.94	15.051	220.01
423.00	10.142	2554.82	10.636	200.88
403.07	6.838	3884.68	7.268	186.48
383.06	4.318	6248.29	4.755	175.23
	x_1 = 0.0913			
487.41	28.324	490.10	28.578	345.59
484.11	26.795	630.98	27.352	287.35
473.05	22.494	926.94	23.322	241.32
463.04	19.160	1192.63	20.075	223.49
443.02	13.684	1854.66	14.645	200.96
423.00	9.531	2854.78	10.446	185.65
403.07	6.411	4227.32	7.230	174.44
383.06	4.122	6447.19	4.819	163.16

Estimation of the Critical Azeotropes. Figure 4 is a plot of log P^A vs. log (x_1^A) for the PFMCH–*n*-hexane system and serves to illustrate the method that was employed to estimate the critical azeotropes. The data in Figure 4 fall very close to a straight line from the lowest to the highest pressures. By the extension of this straight line to the critical locus curve, the critical azeotrope for the system can be approximated. The quantities marked with an asterisk in Table VI represent the critical azeotropes obtained in this manner.

The critical azeotrope must not be confused with the minimum temperature point in the T_c vs. x_1 curve. Thus, in the PFMCH–*n*-hexane system, the critical azeotrope is seen to occur at a mole fraction of 0.464 and not at the minimum critical temperature, where x_1 = 0.550.

Table IV. Perfluoromethylcyclohexane (1)–2,3-Dimethylbutane (2) Data

	dew point		bubble point	
temp, K	press., bar	vol, cm³ mol⁻¹	press., bar	vol, cm³ mol⁻¹
	x_1 = 0.8173			
477.87	21.547	633.61	21.836	490.77
473.10	19.570	920.74	20.563	364.86
463.04	16.201	1353.59	17.727	317.19
453.09	13.695	1704.46	15.164	290.46
443.02	11.294	2193.61	12.930	272.95
423.00	7.600	3570.24	9.185	250.50
403.11	4.952	5658.95	6.359	235.05
383.10	3.059	9132.12	3.580	222.07
	x_1 = 0.5930			
472.11	23.118	553.57	23.237	425.32
468.10	21.260	786.47	21.989	337.73
463.04	19.443	972.28	20.389	308.13
453.09	16.347	1314.48	17.486	277.66
443.02	13.669	1697.57	14.899	268.27
423.00	9.185	2798.61	10.629	235.69
403.07	5.998	4496.77	7.379	220.03
383.07	3.802	7172.72	4.976	207.70
	x_1 = 0.4417			
471.72	24.210	512.22	24.289	398.93
468.1	22.735	715.98	23.002	319.78
463.04	20.873	887.73	21.259	291.56
453.09	17.695	1190.17	18.103	264.63
443.02	14.913	1532.68	15.393	245.51
423.00	10.975	2410.94	10.870	222.30
403.07	6.946	3796.65	7.446	208.79
383.06	4.331	6241.12	4.941	197.40
	x_1 = 0.2875			
475.78	25.943	483.47	26.069	335.82
473.11	24.809	612.22	25.081	295.03
463.04	21.163	887.37	21.530	249.47
453.09	18.028	1152.21	18.406	229.72
443.01	15.224	1465.04	15.665	217.32
423.00	10.703	2244.57	11.101	198.49
403.07	7.253	3472.68	7.695	184.27
383.06	4.748	5364.96	5.124	176.27
	x_1 = 0.2030			
481.31	27.498	490.00	27.629	356.15
478.10	26.091	632.69	26.457	296.18
473.10	24.065	785.50	24.564	269.05
463.04	20.588	1039.52	21.136	243.53
453.09	17.553	1314.37	18.112	225.38
443.02	14.858	1643.96	15.402	213.41
423.00	10.454	2434.98	10.973	196.29
403.07	7.127	3793.68	7.578	184.38
383.09	4.639	5879.15	5.050	73.88
	x_1 = 0.1078			
488.77	29.361	468.41	29.597	331.80
484.11	27.230	641.62	27.830	271.16
474.14	23.317	891.97	24.099	236.48
463.05	19.678	1175.26	20.564	217.53
453.07	16.748	1449.75	17.546	205.84
443.02	14.140	1790.57	15.051	196.50
423.00	9.936	2732.23	10.747	182.34
403.07	6.724	4061.59	7.472	171.11
383.06	4.388	6215.12	5.034	161.80

Prediction of Azeotropic Loci

A binary azeotrope is a state in which the pressure, temperature, chemical potentials (or fugacities) of the components, and composition are the same in both liquid and gas. At a given temperature, it is defined by eq 3–5, where the superscripts refer

$$P^G = P^L \quad (3)$$

$$f_1^G = f_1^L \quad (4)$$

$$f_2^G = f_2^G \quad (5)$$

to the vapor and liquid phases. At any temperature, these three

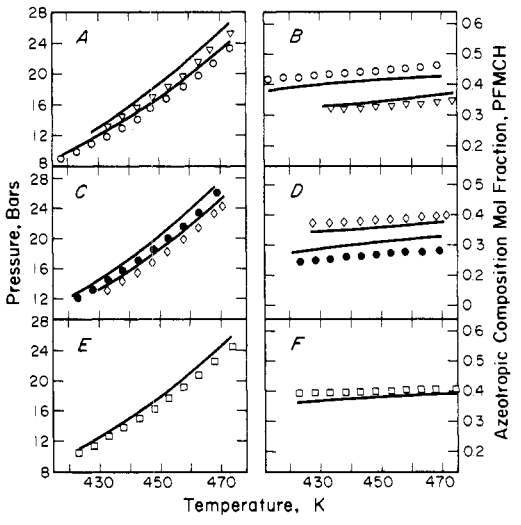

Figure 5. Comparison of experimental and predicted *PT* and *T–x* relations along the azeotropic loci of binary systems of PFMCH with the isomeric hexanes (ξ_{12} = 0.885). Predicted: (—). Experimental data points:

hydrocarbon + PFMCH	*PT* chart	*T–x* chart
(○) *n*-hexane	A	B
(△) 2,3-dimethylbutane	A	B
(◇) 2-methylpentane	C	D
(●) 2,2-dimethylbutane	C	D
(□) 3-methylpentane	E	F

equations may be solved for the three unknowns V^G, V^L, and x, provided expressions are available for the pressure and for the fugacity of each component in the mixture.

In the calculations presented below, the equations for the pressure and for the fugacities were obtained by using the extended form of the corresponding states principle with methane as the reference fluid. The extension of the principle to PFMCH and the hexane isomers required only the critical properties and acentric factors of the pure substances as input parameters. The extension to mixtures was achieved via the van der Waals one-fluid model:

$$T_{cm}V_{cm} = \sum_i \sum_j x_i x_j T_{cij} V_{cij} \quad (6)$$

$$V_{cm} = \sum_i \sum_j x_i x_j V_{cij} \quad (7)$$

and the mixing rules

$$T_{cm} = \xi_{ij}(T_{cii}T_{cjj})^{1/2} \quad (8)$$

$$V_{cm} = (V_{cii}^{1/3} + V_{cjj}^{1/3})^3/8 \quad (9)$$

where the binary interaction coefficient ξ_{ij} is an adjustable constant which must be obtained from experimental data on the mixture. It has been shown earlier (*5*) that values of ξ_{ij} calculated from correlations of critical and azeotropic states and saturated liquid densities (*6*) agree very well with each other, at least for mixtures of the lower molecular weight *n*-alkanes and CO_2. It is convincingly demonstrated here that this is also true for PFMCH–isomeric hexane mixtures. The single value of ξ_{ij} = 0.885 used in *all* calculations presented below was obtained from a correlation of the critical states of the PFMCH–*n*-hexane system. Therefore, there were no adjustable constants used in the calculations reported here. The predicted azeotropic loci shown in Figure 5 were obtained solely from a knowledge of the critical properties and acentric factors of the *pure* components and the critical locus curve of PFMCH–*n*-hexane mixtures. It is seen that agreement between predicted and experimental values is very good. This agreement could be improved further if the critical locus curve of each binary mixture were correlated individually, or if all critical and azeotropic states were correlated simultaneously. It is not the purpose of this study to obtain an "optimum" value of the binary interaction coefficient ξ_{ij}. The calculations were carried out to test the corresponding states approach on the PFMCH–isomeric hexane systems and to look at its predictive capabilities. It is obvious that both of these objectives have been met. It has been shown further that the binary interaction coefficient ξ_{ij} is a property of the forces between molecules in a mixture and its value calculated from one property can be used to predict another (related) property. Further details of the method for the calculation of azeotropic states and of the corresponding states method are given elsewhere (*6*, *7*).

Table V. Perfluoromethylcyclohexane-2,2-Dimethylbutane Data

	dew point		bubble point	
temp, K	press., bar	vol, cm³ mol⁻¹	press., bar	vol, cm³ mol⁻¹
		x_1 = 0.8330		
477.46	21.334	662.67	21.703	476.93
471.10	19.909	875.87	20.821	380.36
463.04	16.316	1323.70	17.698	320.71
453.09	13.511	1758.54	15.139	295.14
443.02	10.805	2387.43	12.872	278.76
423.00	7.473	3678.51	9.107	255.52
403.07	4.832	5818.68	6.245	239.75
383.04	2.928	9564.68	4.174	227.97
		x_1 = 0.6525		
470.10	22.726	595.20	23.057	424.10
463.04	19.862	927.00	20.879	319.89
453.09	16.614	1278.16	17.847	284.42
443.02	13.755	1681.64	15.221	263.72
423.00	9.001	2899.60	10.844	239.05
403.07	6.003	4469.29	7.542	224.10
383.10	3.686	7349.44	4.989	212.32
		x_1 = 0.4024		
467.51	24.483	550.05	24.676	378.50
463.02	22.667	751.04	23.164	313.26
453.09	19.209	1058.71	19.810	271.74
443.02	16.197	1383.29	16.936	251.22
423.00	11.148	2246.97	12.118	226.02
403.07	7.382	3625.92	8.427	209.16
383.07	4.948	1440.20	5.736	197.79
		x_1 = 0.2943		
469.63	25.786	471.14	25.813	383.46
463.06	23.175	746.24	23.451	283.83
453.06	19.701	1024.75	20.058	252.14
443.02	16.752	1310.86	17.118	234.46
423.00	11.793	2060.53	12.342	212.86
403.07	8.061	3204.06	8.561	197.70
383.09	5.309	4953.15	5.782	186.53
		x_1 = 0.2056		
473.10	27.018	491.50	27.138	365.25
468.10	24.942	686.67	25.315	285.82
463.04	23.095	822.21	23.551	266.03
453.09	19.698	1086.10	20.233	239.16
443.02	16.707	1382.52	17.284	222.92
422.99	11.721	2144.62	12.375	204.60
403.07	8.152	3273.07	8.708	189.83
382.24	5.346	4971.73	5.816	176.10
		x_1 = 0.0848		
481.05	28.926	501.73	29.080	321.84
478.10	27.607	603.28	27.885	283.21
473.1	25.690	734.85	25.993	256.49
463.06	22.035	990.06	22.367	230.53
453.11	18.779	1230.89	19.240	215.32
443.02	15.917	1550.74	16.443	205.17
422.99	11.246	2357.04	11.749	189.14

Glossary

A, *B*	constants
a, *b*	constants
f	fugacity

Table VI. Azeotropic PT-x_1^A Data[a]

T, K	P, bar	x_1^A
Perfluoromethylcyclohexane–*n*-Hexane		
398.16	5.954	0.405
403.16	6.612	0.415
408.16	7.318	0.411
413.16	8.101	0.416
418.16	8.878	0.419
423.16	9.828	0.427
428.16	10.810	0.428
433.16	11.798	0.433
438.16	12.897	0.436
443.16	14.084	0.440
448.16	15.467	0.446
453.16	16.752	0.448
458.16	18.255	0.451
463.16	19.771	0.455
468.16	21.408	0.457
473.16	23.232	0.463
473.46*	23.273*	0.464*
Perfluoromethylcyclohexane–3-Methylpentane		
398.16	6.422	0.384
403.16	7.106	0.386
408.16	7.859	0.387
413.16	8.672	0.389
418.16	9.519	0.395
423.16	10.430	0.392
428.16	11.443	0.394
433.16	12.529	0.395
438.16	13.665	0.396
443.16	14.871	0.398
448.16	16.163	0.399
453.16	17.547	0.401
458.16	19.032	0.403
463.16	20.647	0.404
468.16	22.374	0.405
474.36*	24.201*	0.407*
Perfluoromethylcyclohexane–2-Methylpentane		
398.16	6.709	0.353
403.16	7.419	0.357
408.16	8.185	0.359
413.16	9.014	0.362
418.16	9.904	0.364
423.16	10.865	0.367
428.16	11.911	0.372
Perfluoromethylcyclohexane–2-Methylpentane		
433.16	13.032	0.377
438.16	14.202	0.379
443.16	15.449	0.381
448.16	16.793	0.384
453.16	18.246	0.386
458.16	19.828	0.389
463.16	21.450	0.390
468.16	23.199	0.395
471.36*	24.339*	0.399*
Perfluoromethylcyclohexane–2,3-Dimethylbutane		
398.16	6.785	0.289
403.16	7.488	0.293
408.16	8.272	0.300
413.16	9.116	0.301
418.16	9.993	0.304
423.16	10.936	0.308
428.16	11.980	0.310
433.16	13.101	0.318
438.16	14.267	0.320
443.16	15.504	0.325
448.16	16.832	0.327
453.16	18.269	0.330
458.16	19.837	0.333
463.16	21.445	0.338
468.16	23.217	0.343
473.86*	25.279*	0 348*
Perfluoromethylcyclohexane–2,2-Dimethylbutane		
398.16	7.652	0.220
403.16	8.452	0.227
408.16	9.290	0.230
413.16	10.175	0.234
418.16	11.112	0.239
423.16	12.142	0.243
428.16	13.263	0.248
433.16	14.476	0.252
438.16	15.738	0.257
443.16	17.076	0.262
448.16	18.510	0.266
453.16	20.023	0.271
458.16	21.660	0.274
463.16	23.435	0.275
469.26*	26.063*	0.279*

[a] The asterisks denote critical azeotropes.

Table VII. Azeotropic A and B Constants for a Least-Squares Analysis of Eq 1

system	azeotropic constant A	azeotropic constant B	std dev[a]
PFMCH–*n*-hexane	4.457 560	−1466.323	0.008 707
PFMCH-2-MP	4.445 572	−1442.199	0.003 733
PFMCH-3-MP	4.438 409	−1446.563	0.003 889
PFMCH-2,2-DMB	4.365 985	−1387.717	0.003 920
PFMCH-2,3-DMB	4.419 434	−1429.826	0.003 728

[a] Standard deviation is the square root of the sum of the squares of of the residuals, divided by the number of data points minus two.

Table VIII. Azeotropic a and b Constants for a Least-Squares Analysis of Eq 2

system	azeotropic constant a	azeotropic constant b	std dev
PFMCH–*n*-hexane	4.724 130	10.044 05	0.023 45
PFMCH-2-MP	5.733 198	10.836 50	0.015 89
PFMCH-3-MP	10.404 90	23.100 01	0.031 01
PFMCH-2,2-DMB	4.143 642	4.980 282	0.014 34
PFMCH-2,3-DMB	4.782 693	7.330 248	0.018 44

P	pressure
R	gas constant
T	thermodynamic temperature
V	volume
x	mole fraction
ρ	density
ξ	binary interaction coefficient

Subscripts

1, 2	component 1, 2
c	critical value
cm	pseudocritical value for mixture
i, j	component i, j

Superscripts

A	azeotropic value
G	gas
L	liquid

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