c = critical
cm = pseudo-critical
i,j = component i,j
x,V = differentiation with respect to x,V

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Part II. Vapor-Liquid Equilibria and Azeotropic States of Propane-Perfluorocyclobutane Mixtures

Measurement of vapor-liquid equilibria and azeotropic states of propane-perfluorocyclobutane mixtures are reported in this paper. The propane-perfluorocyclobutane system exhibits positive azeotropic behavior which persists in the critical region of the system. The prediction of vapor-liquid equilibria and of the locus of azeotropic points using an extended corresponding states principle is also reported. The predictions require information obtained solely from a study of the critical states of the system.

SCOPE

The study of the phase behavior of non-ideal mixtures which exhibit azeotropic behavior in their critical regions is of great practical as well as theoretical interest. In Part I of this paper, we showed that the critical locus curve of the propane-perfluorocyclobutane system exhibits a minimum temperature point, this behavior being characteristic of mixtures that form positive critical azeotropes. The critical locus curve forms the boundary between the single phase and the two-phase regions. The objective of this work was to extend our previous measurements of the critical region into the two-phase region of the phase diagram.

A second objective of the work was to test the predictive capabilities of an extension of the corresponding states principle in order to show how information obtained from the study of the critical locus curve may be used to predict vapor-liquid equilibria and the azeotropic locus.

CONCLUSIONS AND SIGNIFICANCE

Dew and bubble point measurements for pure propane, pure perfluorocyclobutane and seven of their mixtures are reported in this paper. The temperature range of the data extended from 328.15 to 398.15°K and pressure from approximately 100 to 6900

kPa. The data have been used to determine the *P-T-x* coordinates of the azeotropic locus of the propane-perfluorocyclobutane system between 328.15°K and the critical azeotropic temperature of 365.09°K.

Vapor-liquid equilibria and the azeotropic locus of the system have been predicted using an extended Corresponding States Principle. A binary interaction coefficient required in the calculations was obtained from the correlation of the critical states of the system. The calculations demonstrate how information obtained from a study of one part of the phase diagram may be used to predict other parts of the diagram.

INTRODUCTION

An investigation of the volumetric and phase behavior of the propane-perfluorocyclobutane system was undertaken as part of a continuing study of the phase diagrams of mixtures that form azeotropes in the critical region. The critical locus curve of the propane-perfluorocyclobutane system and its correlation using an extended corresponding states principle were reported in part I of this paper (Barber et al., 1980). It was found that the critical locus exhibits a minimum temperature point which is characteristic of systems which form positive azeotropes in their critical region. It was shown further that all critical properties (T_c, V_c, P_c) of propane-perfluorocyclobutane mixtures could be correlated by the extended corresponding states method using only a single binary interaction coefficient ($\xi_{12} = 0.89$), which was found to be independent of temperature, pressure and composition.

In this paper, we report the measurements of dew and bubble points as well as azeotropic states of propane-perfluorocyclobutane mixtures. The predictive capabilities of the extended corresponding states method are tested further and the method is used for the calculation of vapor-liquid equilibria and azeotropic states, using a value of the binary interaction coefficient ($\xi_{12} = 0.89$) obtained in Part I of this paper.

EXPERIMENTAL

The experimental details have been reported in Part I and are not repeated here. The accuracy and precision of the measured values have also been reported in Part I.

RESULTS

Dew and bubble points were determined for pure propane and pure perfluorocyclobutane and for seven binary mixtures. Figure 1 graphically summarizes the data on a *P-T-x* plot. Several mixtures at low concentrations of perfluorocyclobutane ($x < 0.25$) were examined in order to clearly define the curvature of the critical locus in this region. The temperature of the data ranged from 328.15 to 398.15°K and pressure from approximately 100 to 6895 kPa. Selected data points for the two pure components and seven binary mixtures are presented in Table 1.

The saturated data for perfluorocyclobutane were compared with those of Martin (1962). At selected temperatures, the pressure agreed within 10kPa, saturated liquid volumes within 0.002 m^3 $kmol^{-1}$ and saturated vapor volumes within 0.005 m^3 $kmol^{-1}$. This agreement is well within the experimental precision of the data. Saturation data for propane were compared with those of Deschner and Brown (1941) and Matsche and Thodos (1962). In this case, pressures agreed within 10 kPa, saturated liquid volumes within 0.001 m^3 $kmol^{-1}$ and saturated vapor volumes within 0.003 m^3 $kmol^{-1}$. The overall agreement of the propane data was considered good.

The azeotropic pressure and composition were determined at various temperatures between 328.15 and 358.15°K by drawing smooth curves through the dew and bubble points at those temperatures. For each temperature, the maxima on these curves could reliably be established. It was also observed that the maxima of both the dew and bubble point curves occurred at approximately the same composition. An average of the two values was taken as the azeotropic pressure and composition. The results are presented in Table 2. By extension of the azeotropic locus to the critical locus (Genco et al., 1980b), the coordinates of the critical azeotrope were also estimated. These are marked with an asterisk in Table 2.

PREDICTION OF VAPOR-LIQUID EQUILIBRIA AND AZEOTROPIC STATES

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 the liquid and gas phases. At a given temperature, it is given by:

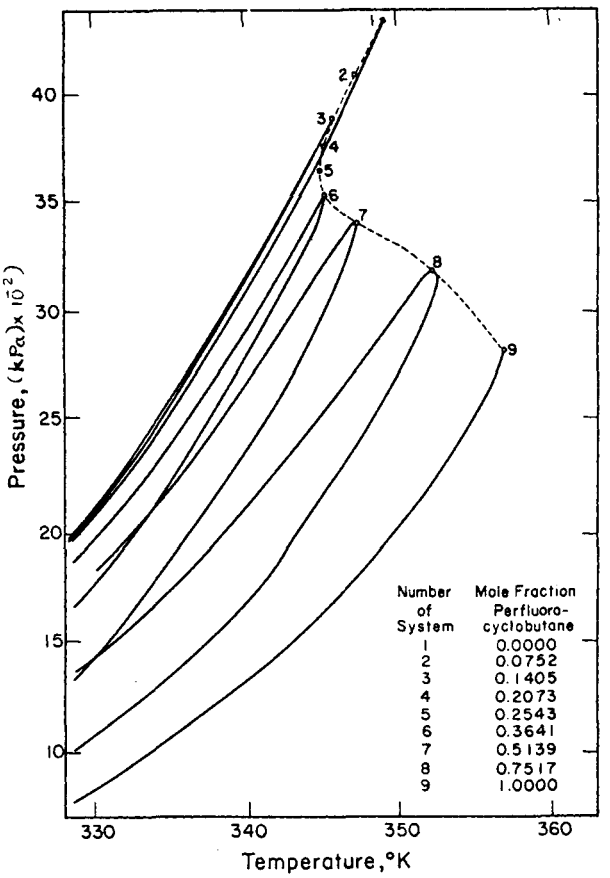

Figure 1. Vapor-liquid equilibria in the propane-perfluorocyclobutane system.

TABLE 1. DEW AND BUBBLE POINTS IN THE PROPANE (1)-PERFLUOROCYCLOBUTANE (2) SYSTEM.

	Dew Point		Bubble Point	
T(°K)	$P(kPa)$	$V(m^3kmol^{-1})$	$P(kPa)$	$V(m^3kmol^{-1})$
		$x_2 = 0.000$		
329.41	1935	0.9776	1948	0.1017
338.42	2335	0.7781	2345	0.1047
348.57	2853	0.5965	2865	0.1125
353.99	3161	0.5084	3169	0.1176
359.97	3529	0.4195	3533	0.1256
364.88	3868	0.3456	3878	0.1368
368.19	4104	0.2883	4108	0.1498
369.28	4188	0.2602	4192	0.1596
369.92	4232	0.2376	4233	0.1715
		$x_2 = 0.0752$		
329.41	1946	0.9413	1971	0.1046
338.42	2355	0.7356	2372	0.1105
348.57	2883	0.5585	2904	0.1193
353.50	3172	0.4752	3187	0.1254
359.97	3575	0.3757	3589	0.1371
361.38	3671	0.3532	3685	0.1415
364.35	3883	0.2959	3894	0.1548
366.17	4017	0.2418	4023	0.1837
		$x_2 = 0.1405$		
329.41	1952	0.9349	1967	0.1128
338.42	2354	0.7359	2366	0.1192
348.57	2887	0.5468	2897	0.1295
353.99	3201	0.4544	3212	0.1388
359.97	3580	0.3482	3588	0.1561
361.87	3715	0.3050	3721	0.1677
363.05	3801	0.2649	3802	0.1836
363.27	3816	0.2530	3817	0.1903
		$x_2 = 0.2073$		
329.41	1897	0.9429	1959	0.1146
338.42	2300	0.7337	2336	0.1202
348.57	2836	0.5390	2862	0.1317
353.99	3150	0.4436	3166	0.1412
359.97	3530	0.3298	3545	0.1644
360.73	3591	0.3118	3604	0.1689
361.64	3658	0.2837	3668	0.1790
		$x_2 = 0.2543$		
329.41	1836	1.0108	1919	0.1214
338.42	2230	0.7850	2304	0.1288
348.57	2758	0.5717	2821	0.1414
353.99	3078	0.4672	3127	0.1529
357.47	3299	0.3978	3338	0.1635
359.97	3467	0.3374	3496	0.1784
360.67	3519	0.3151	3539	0.1860
361.33	3566	0.2885	3585	0.1977
		$x_2 = 0.3641$		
329.41	1639	1.1334	1842	0.1226
338.42	2037	0.8625	2212	0.1303
348.57	2542	0.6313	2699	0.1429
353.44	2837	0.5247	2969	0.1510
356.51	3028	0.4593	3143	0.1601
359.97	3256	0.3807	3341	0.1749
361.29	3345	0.3456	3422	0.1870
362.42	3442	0.2972	3484	0.2092
		$x_2 = 0.5139$		
329.41	1298	1.5353	1696	0.1299
338.42	1703	1.0995	2039	0.1363
348.47	2163	0.8022	2475	0.1478
353.99	2454	0.6628	2746	0.1569
359.97	2817	0.5191	3053	0.1720
361.89	2943	0.4741	3151	0.1800
364.44	3127	0.4036	3288	0.1975
365.95	3256	0.3453	3353	0.2290
		$x_2 = 0.7517$		
329.41	987	2.0831	1342	0.1371
338.42	1221	1.6333	1612	0.1423
348.57	1538	1.2319	1960	0.1509
359.97	2061	0.8703	2424	0.1659
368.19	2481	0.6406	2796	0.1843
371.88	2696	0.5428	2961	0.1983
375.44	2940	0.4320	3118	0.2316
376.46	3024	0.3923	3137	0.2625
		$x_2 = 1.000$		
329.41	750	2.9157	762	0.1477
338.42	947	2.2828	963	0.1534
348.57	1205	1.7288	1214	0.1597
359.99	1538	1.2727	1550	0.1704
368.19	1847	0.9986	1856	0.1789
377.99	2258	0.7251	2267	0.1994
387.74	2751	0.4208	2758	0.2605

$$P^G = P^L \tag{1}$$

$$f_1^G = f_1^L \tag{2}$$

$$f_2^G = f_2^L \tag{3}$$

$$x_1^G = x_1^L \tag{4}$$

$$(\text{or } y_1 = x_1)$$

At any temperature, Eqs. 1–3 may be solved for the three unknowns V^G, V^L and x_1, provided expressions are available for the pressure and for the fugacity of each component in the mixture.

Equation 4, of course, holds only for azeotropic states. For the general vapor-liquid equilibrium problem, two quantities (T and P in this work) must be specified, and the following equations:

$$P = P^G \tag{5}$$

$$P = P^L \tag{6}$$

$$f_1^G = f_1^L \tag{7}$$

$$f_2^G = f_2^L \tag{8}$$

must be solved for the four unknowns V^G, V^L, x_1 and y_1.

In the calculations presented below, the equations for the pressure and for the fugacities were obtained using the extended form of the corresponding states principle with methane as the reference fluid (Teja and Rowlinson, 1973; Teja and Kropholler, 1975; Teja 1975, 1979). The method requires only the critical properties and acentric factors of the pure fluids as input parameters. The extension to mixtures was achieved via the van der Waals one-fluid model:

$$T_{cm}V_{cm} = \sum_i \sum_j x_i x_j T_{cij} V_{cij} \tag{9}$$

$$V_{cm} = \sum_i \sum_j x_i x_j V_{cij} \tag{10}$$

TABLE 2. AZEOTROPIC PROPERTIES FOR THE PROPANE (1)-PERFLUOROCYCLOBUTANE (2) SYSTEM

T(°K)	P^{Az}(kPa)	x_2^{Az}
328.15	1923	0.105
333.15	2131	0.102
338.15	2362	0.105
343.15	2612	0.103
348.15	2884	0.104
353.15	3177	0.103
358.15	3480	0.103
365.09*	3936*	0.104*

* Critical azeotrope (estimated).

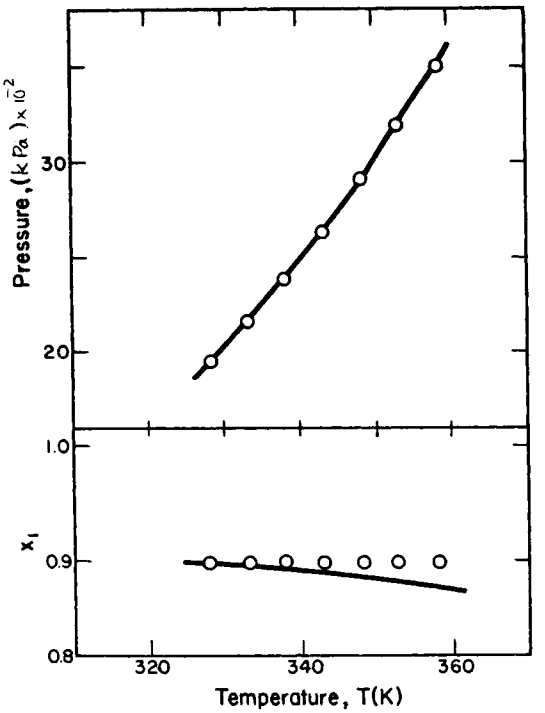

Figure 2. The azeotropic locus of the propane-perfluorocyclobutane system. The solid line is the predicted curve with $\xi_{12} = 0.89$. Experimental points are denoted by circles.

and the mixing rules:

$$T_{cij} = \xi_{ij} (T_{cii} T_{cjj})^{1/2} \tag{11}$$

$$V_{cij} = (V_{cii}^{1/3} + V_{cjj}^{1/3})^3/8 \tag{12}$$

where the binary interaction coefficient ξ_{ij} is an adjustable constant which must be obtained from some experimental data on the mixture. It has been shown earlier (Teja, 1978) that values of ξ_{ij} calculated from correlations of critical and azeotropic states and saturated liquid densities (Teja, 1975) agree with each other and with values obtained from a correlation of the properties of chemically similar systems (Genco et al., 1980). It is convincingly demonstrated here that a value of ξ_{ij} obtained from a correlation of one property may be used for the prediction of other properties. The single value of $\xi_{ij} = 0.89$ for the propane-perfluorocyclobutane system used in all calculations presented below was obtained from the correlation of the critical states of the system (Barber et al., 1980). Therefore, there were no adjustable constants used in the calculations reported in this work. The predicted azeotropic locus is shown in Figure 2. The predictions have been extended further to vapor-liquid equilibria at conditions well away from the critical region (Figure 3). It is seen that agreement between prediction and experiment is satisfactory and, to a good approximation, the binary interaction coefficient does not vary with temperature, pressure and composition. Agreement between prediction and experiment can, of course, be improved if both critical and azeotropic states are correlated simultaneously. This was not, however, attempted in this study to test the predictive capabilities of the method. Agreement can also be improved if shape factors for perfluorocyclobutane are obtained from the data. We have, however, preferred to use the shape factors for the n-alkanes correlated by Leland and Chappelear (1968) in our method to test the limits of these correlations. There is, therefore, a certain degree of inherent error in the calculations because the properties of perfluorocyclobutane do not conform to the properties of the reference substance (methane).

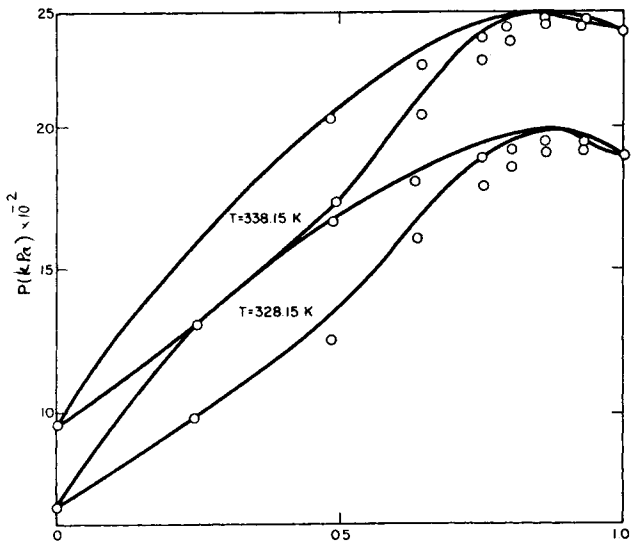

Figure 3. A comparison of experimental and predicted vapor-liquid equilibria in the propane-perfluorocyclobutane system. The solid lines are the predicted curves with $\xi_{12} = 0.89$. Experimental points are denoted by circles.

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AST wishes to thank the faculty and staff of The Ohio State University for their hospitality during the summer 1980.

NOTATION

f	= Fugacity
P	= pressure
R	= gas constant
T	= thermodynamic temperature
V	= volume
x	= mole fraction
y	= mole fraction (in the vapor phase)
ξ	= binary interaction constant

Subscript

1,2	= component 1,2
c	= critical value
cm	= pseudocritical value
i,j	= component i,j

Superscript

G	= gas phase
L	= liquid phase

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Part. III. *P-V-T-x* Data and Second Virial Coefficients of Propane-Perfluorocyclobutane Mixtures

P-V-T-x **data for the propane-perfluorocyclobutane system are reported in this paper. The data cover a temperature range from 329.4 to 397.7°K and a pressure range from 60 to 6920 kPa. The low pressure compressibility measurements were used to determine second virial coefficients of pure propane and pure perfluorocyclobutane and for seven of their mixtures. The prediction of second virial coefficients using an extended corresponding states principle is also reported. Excellent predictions of the second virial coefficients of both pure components and mixtures have been obtained using, in the case of mixtures, a binary interaction coefficient obtained from a study of the critical states of the system.**

SCOPE

It is often convenient to represent the volumetric and thermodynamic properties of gases and gas mixtures by the virial equation of state. Virial coefficients are also of interest because they provide a link between experimental measurements and intermolecular forces.

An objective of our work was to extend our measurements of the critical states and vapor-liquid equilibria in the propane-perfluorocyclobutane system to the single phase regions of the phase diagram. The gas phase compressibility measurements may then be used to obtain second virial coefficients for the system. More generally, our objective was to obtain comprehensive data for mixtures that exhibit positive azeotropic behavior in their critical region. Critical states and vapor-liquid equilibria in the propane-perfluorocyclobutane system have already been reported by us in Parts I and II of this work.

A second objective of this work was to use our second virial coefficient data to test the predictive capabilities of an extended Corresponding States Principle. It is well known that Corresponding States methods may be used to correlate second virial coefficients. However, our aim was to see if our method was capable of predicting second virial coefficients of both pure components and mixtures using, in the case of mixtures, information obtained from a study of their critical states.

CONCLUSIONS AND SIGNIFICANCE

Volumetric data for the propane-perfluorocyclobutane system covering a temperature range from 329.4 to 397.7°K and a pressure range from 60 to 6920 kPa are reported in this paper. The low pressure measurements have been used to determine second virial coefficients for both the pure components and seven of their mixtures over the temperature range studied. This data set completes our comprehensive measurements of the volumetric and phase behavior of the propane-perfluorocyclobutane system. The data presented in the three papers in this series cover the gas phase, the two phase region, the critical region and the liquid phase region of this highly non-ideal system, which exhibits positive azeotropic behavior up to its citical region.

We have used our data to test the ability of an extended Corresponding States Method to correlate and predict a major part of the phase diagram of the propane-perfluorocyclobutane system. We have already shown how a binary interaction coefficient obtained from a study of the critical states of the system may be used to predict the azeotropic locus and vapor-liquid equilibria in the system. We have extended the Corresponding States method here to second virial coefficients of both pure fluids and mixtures. We show below how second virial coefficients may be predicted using a value of the binary interaction coefficient obtained from our study of the critical states. It therefore seems feasible that the extended Corresponding States Principle may be used to predict the complete phase diagram of mixtures using information obtained from the more readily available second virial coefficients.