dation Grant ENG 77-15953 is gratefully acknowledged. We thank the Calgon Corp. for providing activated carbon.

NOTATION

$A_i(n)$ = Sucrose adsorbed after nth regeneration, kg
$A_i'(n)$ = Sucrose adsorbed after nth regeneration and after drying in the oven for 15 hours, kg
i = Number of reactor tube
k_1 = Rate constant for steam-carbon reaction Eq. 1, kg/(kg)(s)(Pa)
k_2,k_3 = Parameters in rate equation, Pa^{-1}
n = Number of regenerations; $n = 0$ indicates conditions after initial heat treatment
p_{H_2}, p_{H_2O} = Partial pressures of hydrogen and steam, Pa
$P_i(n)$ = Pore volume after n-th regeneration, m^3
R = Rate of steam-carbon reaction, (kg of carbon reacted/(kg of virgin carbon unburned) (s)
R_g = Gas constant, kJ/(mol) (°K)
$S_i(n)$ = Surface of carbon in the ith tube after the nth regeneration, m^2
T = Temperature, °K
$W_i(n)$ = Weight of carbon in reactor tube i after the nth regeneration, kg

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A Study of the Volumetric and Phase Behavior of Binary Systems

Part I: Critical Properties of Propane-Perfluorocyclobutane Mixtures

The volumetric and phase behavior of propane-perfluorocyclobutane mixtures has been determined in the critical region. This system exhibits a minimum temperature point in its critical locus curve and forms a positive critical azeotrope. The measured critical points in this system and their correlation using an extended corresponding states principle are reported in this paper.

J. R. BARBER
W. B. KAY
and A. S. TEJA

Department of Chemical Engineering
The Ohio State University
Columbus, OH 43210

SCOPE

The study of the volumetric and phase behavior of mixtures, in addition to yielding fundamental information on molecular interactions, is of great practical interest in chemical engineering operations. Of particular interest are non-ideal mixtures which exhibit azeotropic behavior over considerable ranges of pressure and temperature. In 1951, this laboratory began a study of azeotrope-forming systems which indicated that their phase diagrams may exhibit a great variety of forms depending on the differences in size, shape and chemical nature of the components. Further evidence of this variety of behavior is presented here in the study of the propane-perfluorocyclobutane system. This system was chosen principally because the critical pressures and temperatures of the components are relatively low, making it possible to span a considerable range of reduced pressures and temperatures with our apparatus. Our measurements therefore cover a major part of the phase diagram of this system—from second virial coefficients and vapor densities through vapor-liquid equilibria and critical states to compressed liquid densities. One objective of this work was to make available this range of self-consistent data for testing methods of prediction.

A. S. Teja is presently with School of Chemical Engineering, Georgia Institute of Technology, Atlanta, GA 30332; J. R. Barber, with Union Carbide, Yorktown, NY.

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A second objective of our work was to test the predictive capabilities of the extended Corresponding States Principle (with shape factors). We will demonstrate how information obtained from one part of the phase diagram may be used to make quantitative predictions of properties in other parts of the diagram.

CONCLUSIONS AND SIGNIFICANCE

Critical states of the propane-perfluorocyclobutane system have been measured and are presented in this paper. The critical locus curve of this system exhibits a minimum in temperature which is characteristic of mixtures which form positive critical azeotropes.

The critical properties have been correlated using an extension of the Corresponding States Principle. A single value of a binary interaction coefficient is sufficient to correlate all the critical properties of the system. For the seven mixtures studied, critical temperatures can be correlated with average absolute deviations of 0.8°K, critical pressures with average absolute deviations of 60 kPa and critical volumes with average absolute deviations of 0.001 m^3 $kmol^{-1}$ using a value of 0.89 for the binary interaction coefficient. Subsequent papers will show that this value may be used to make quantitative predictions of vapor-liquid equilibria, the azeotropic locus and volumetric properties of the system.

INTRODUCTION

In earlier work in this laboratory on the volumetric and phase behavior of binary systems that form azeotropes in the critical region, the diversity of the shape of the *P-T-x* diagrams was pointed out and shown to depend on the shape of the critical locus curve. An investigation of binary systems composed of the n-alkanes with perfluoro-n-heptane (Jordan and Kay, 1963) and with acetone (Kay, 1964) as common components, and the isomers of n-hexane with perfluoromethylcyclohexane as the common component (Genco et al., 1980), showed that the shape of the critical locus curve depends on the difference between the critical properties of the pure components and on the relative strength of the unlike pair interactions in the mixture. In a continuation of the study of these non-ideal systems (Barber, 1968) the range of pressure, temperature and volume has been extended in this work to include the compressibility of the vapor and liquid in and around the critical region. The system that was studied, propane-perfluorocyclobutane, was chosen principally because the critical pressures and temperatures of the pure components were relatively low, making it possible to attain high reduced pressures and temperatures with the apparatus employed.

The propane-perfluorocyclobutane system was found to exhibit positive azeotropic behavior which persisted into the critical region. Critical states of this system and their correlation using an extended corresponding states principle are reported here. Measurements and predictions of dew and bubble points, as well as azeotropic states of these mixtures are reported in the second part of the paper. *P-V-T-x* data in the vicinity of the critical region, as well as derived properties such as second virial coefficients, are reported in the final part of this paper.

EXPERIMENTAL

The *P-V-T-x* relations of the propane-perfluorocyclobutane system were obtained by the experimental determination of a set of *P-V* isotherms for a series of mixtures ranging in composition from pure propane to pure perfluorocyclobutane. For each isotherm, a series of pressure-total volume measurements were taken at decreasing volumes—from the volume occupied by the expanded vapor phase, through the two-phase region, to the volume occupied by the compressed liquid phase. The apparatus and experimental procedures were essentially those used in previously reported studies (Kay, 1946; Kay and Rambosek, 1953; Kay and Donham, 1965).

Briefly, a small air-free sample of the liquid was confined over mercury in a thick-wall glass tube, which was surrounded by a constant temperature jacket. The temperature was maintained constant by the condensing vapor of a series of pure organic liquids heated at a constant and controlled pressure in a side-arm flask attached to the jacket. The experimental tube was held rigidly in a mercury-filled compressor block with means provided for controlling and measuring the pressure on the sample.

The volume of the sample was determined by the measurement of the length of the tube occupied by the sample, the length having been related to the volume by a previous calibration of the tube. To bring about equilibrium quickly, the sample was stirred by a steel ball-bearing which had been inserted in the tube prior to loading the sample. The bearing was moved rapidly through the sample by a magnet around the outside of the constant temperature jacket.

The experimental tube was constructed from three sections of precision-bore, heavy-walled glass tubing of different internal diameters. The dimensions of the tube are shown in Figure 1. The total volume of the tube and of each section were such that the isothermal compressibility of the vapor at low pressures and of the liquid at high pressures could be determined with a single sample. The tube was calibrated by evacuating and filling it with mercury at 298.15°K. With the tube mounted vertically, small amounts of mercury were removed, weighed and the length of the tube occupied was measured to ±0.0001 cm with a precision cathetometer, until all mercury was removed. The volume of each increment was calculated from the mass and density of the mercury. Regression equations relating the volume of the tube to the distance from the sealed end were then derived for each of the three sections. The calibration was performed twice and was considered satisfactory when the two sets of data agreed to within the experimental error.

The temperature of the vapor jacket surrounding the experimental tube was measured within ±0.01°K with a calibrated copper-constantan thermocouple whose output was balanced against a sensitive potentiometer. The thermocouple was calibrated by comparison at 18 temperatures between 306.15°K and 143.15°K with a platinum resistance thermometer which had been calibrated at the National Bureau of Standards. A regression equation was derived expressing the millivolt output of the thermocouple in terms of the temperature.

The sample pressure in the vapor region up to 276 kPa was measured with a mercury manometer; at higher pressures, a dead weight gauge with a sensitivity of 0.3 kPa was used. The pressure along the saturated liquid and vapor curves and in the compressed liquid region was measured with a precision spring gauge with a 40 cm dial. This gauge covered a range from 0 to 13800 kPa in 13.8 kPa intervals. Both the dead weight and spring gauges were compared with a standard dead weight gauge.

The results of an extended statistical analysis of experimental errors are summarized in Table 1.

Sources and Purity of Materials and Preparation of Mixtures

The propane was supplied by the Phillips Petroleum Company with a reported purity of 99.9+ mole %. The perfluorocyclobutane was supplied by the E.I. DuPont de Nemours Company also with a reported purity of 99.9+ mol %. Both compounds were distilled and degassed at low pressure and stored in sealed glass ampoules until ready for use, each ampoule

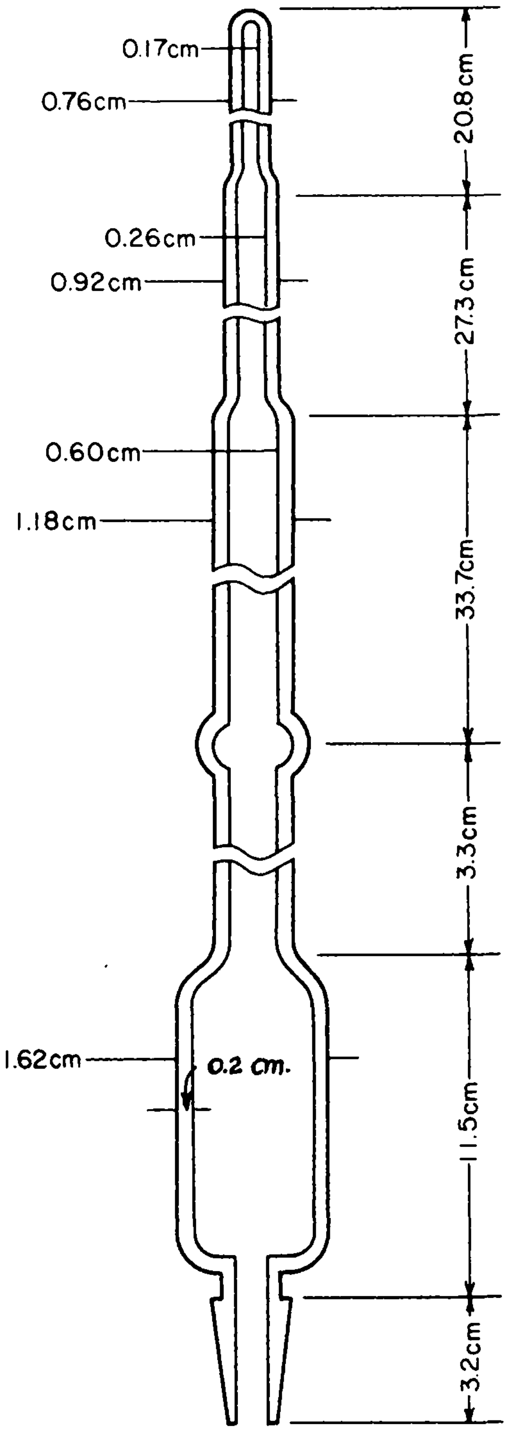

Figure 1. Dimensions of the experimental tube.

containing slightly more than the required quantity of the vapor for one loading of the experimental tube.

Mixtures were prepared by first filling the experimental tube under vacuum with mercury and then injecting into the tube, by means of a micro-gas burette, a measured volume of each of the gases at a known temperature and pressure. The micro-gas burette consisted essentially of a calibrated section of precision glass capillary connected to a stainless steel bellows and surrounded by a water jacket for temperature control. The calibrated section was 50 cm. long and had a volume of 0.05065 cm^3. An etched scale with lines at 0.1 cm intervals made it possible to read gas volumes to about 0.001 cm^3. The sample mass and the composition of the mixture were determined from isothermal compressibility measurements.

EXPERIMENTAL RESULTS

The following experimental data are presented in this paper:

(i) The critical properties of the pure components

(ii) The critical properties of binary mixtures of propane and perfluorocyclobutane

TABLE 1. ACCURACY AND PRECISION OF EXPERMENTAL DATA

Property	Instrument	Precision	Accuracy
T	Thermocouple	±0.05°K	±0.1°K
P	Heise Pressure Gauge	±2 kPa	±3.0 kPa
P	DWG	±0.03 kPa	±0.1 kPa
P	Hg Manometer	±0.1 kPa	±0.02 kPa
V	1.7 mm Bore Tube	±0.00015 cm^3	±0.0005 cm^3
V	2.6 mm Bore Tube	±0.0003 cm^3	±0.0008 cm^3
V	6.0 mm Bore Tube	±0.001 cm^3	±0.005 cm^3
x		±0.001	
Bubble point, P		±3.0 kPa	
Dew point, P		±14 kPa	
P_c		±17 kPa	

TABLE 2. CRITICAL PROPERTIES OF THE PURE COMPONENTS

T_c	P_c, kPa	V_c (m^3 kmol^{-1})	Ref.
Propane			
370.02	4260	0.1975	This Work
369.72	4261	0.1949	Chun (1964)
369.96	4257	0.1952	Beattie et al. (1937)
369.99	4255	0.2006	Huff and Reed (1963)
369.77	4268	0.1993	Hissong (1965)
Perfluorocyclobutane			
388.43	2785	0.3198	This Work
388.35	2777	0.3248	Douslin et al. (1959)
388.47	2783	0.3227	Martin (1962)

TABLE 3. EXPERIMENTAL CRITICAL PROPERTIES OF PROPANE (1) PERFLUOROCYCLOBUTANE (2) MIXTURES

x_{2c}	T_c (°K)	P_c (kPa)	V_c (m^{3}kmol^{-1})
0.0752	366.21	4025	0.2081
0.1405	363.44	3831	0.2151
0.2073	362.23	3698	0.2223
0.2543	361.81	3596	0.2295
0.3641	362.63	3472	0.2434
0.5139	366.36	3354	0.2587
0.7517	376.69	3132	0.2884

Measurements along the saturation boundaries, azeotropic states and compressibility data are presented in subsequent parts of this work.

Table 2 presents the experimentally determined critical constants of propane and perfluorocyclobutane, together with reliable values obtained from the literature.

Experimentally determined critical properties of propane-perfluorocyclobutane mixtures are given in Table 3.

CORRELATION OF CRITICAL STATES

The critical states measured in this study have been used to extensively test and develop an extended form of the corresponding states principle (Teja and Rowlinson, 1973; Teja and Kropholler, 1975; Teja, 1975, 1979). This method has been used in our earlier work (Genco et al., 1980) for the calculation of critical and azeotropic states of mixtures of perfluoromethylcyclohexane (PFMCH) with the isomers of n-hexane. It was shown that quantitative predictions of the critical and azeotropic states of PFMCH-isomeric hexane systems may be made using information obtained solely from the measured values of the critical states of PFMCH-n-hexane mixtures. It will be shown here that the method can be used not only to predict azeotropic states, but also vapor-liquid equilibria and thermodynamic properties using information obtained from the correlation of critical states.

Briefly, the method starts from the known P-V-T properties of

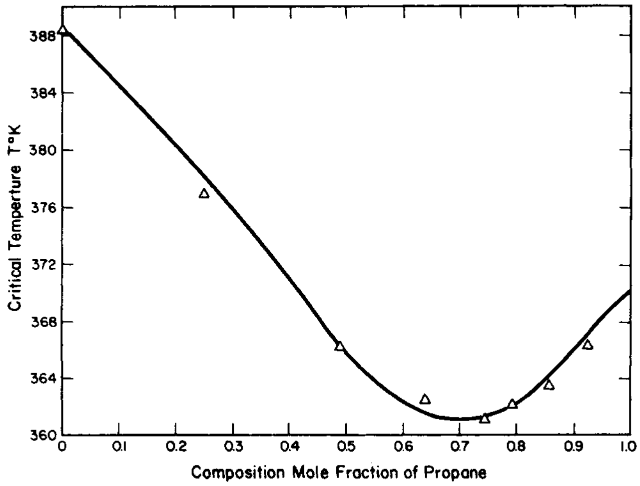

Figure 2. Critical temperature-composition relations of the binary system propane-perfluorocyclobutane. Predicted values with $\xi = 0.89$ are shown by full lines. Experimental points are denoted by Δ.

a reference substance (methane in our study) and yields the properties of any substance which is conformal to the reference substance from a knowledge of its critical properties. Non-conformal substances can be included in the treatment using shape factors (Leland and Chappelear, 1968) whose magnitude is proportional to the difference in acentric factors of that substance and the reference substance. The method can be extended to mixtures via the van der Waals one-fluid model:

$$V_{cm}\, T_{cm} = \sum_i \sum_j x_i\, x_j\, T_{cij}\, V_{cij} \tag{1}$$

$$V_{cm} = \sum_i \sum_j x_i\, x_j\, V_{cij} \tag{2}$$

$$Z_{cm} = \sum_i x_i Z_{cii} \tag{3}$$

The like-terms ($i = j$) are obtained from pure component properties, whereas the unlike terms ($i \neq j$) require some mixture data for their evaluation. The usual procedure is to write (Genco et al., 1980; Leland and Chappelear, 1968):

$$T_{cij} = \xi_{ij}(T_{cii}T_{cjj})^{1/2} \tag{4}$$

$$V_{cij} = (V_{cii}^{1/3} + V_{cjj}^{1/3})^3/8 \tag{5}$$

where the binary interaction coefficient ξ_{ij} is an adjustable constant which must be obtained from experimental data. In general, it is sufficient to characterize each binary system by means of one adjustable coefficient which, to a good approximation, is independent of temperatuare, pressure, and composition. Thus, the binary interaction coefficient calculated from the critical states of a system may be used to make quantitative predictions of azeotropic states and vapor-liquid equilibria in the system at different conditions of temperature, pressure and composition. This will be demonstrated in this and the following papers of this series.

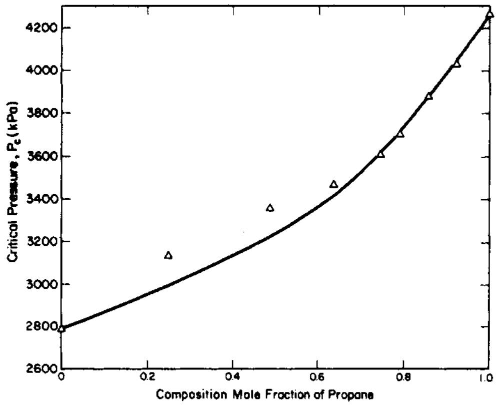

Figure 3. Critical pressure-composition relations of the binary system: propane-perfluorocyclobutane. Predicted values with $\xi = 0.89$ are shown by full lines. Experimental points are denoted by Δ.

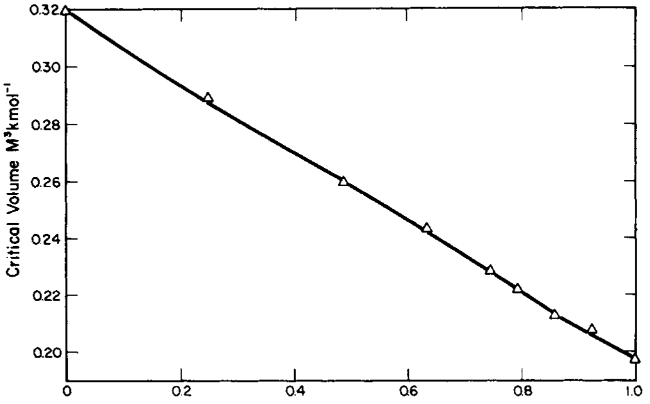

Figure 4. Critical volume-composition relations of the binary system: propane-perfluorocyclobutane. Predicted values with $\xi = 0.89$ are shown by full lines. Experimental points are denoted by Δ.

Critical states of binary mixtures which exhibit azeotropic behavior in the critical region satisfy the following relationships (Teja and Rowlinson, 1973):

$$A_{2x}A_{2v} - A_{xv}^2 = 0 \tag{6}$$

$$A_{3x}A_{2v}^3 - 3A_{2xv}A_{xv}A_{2v}^2 + 3A_{x2v}A_{2v}A_{xv}^2 - A_{3v}A_{xv}^3 = 0 \tag{7}$$

where the subscripts denote derivatives, e.g., $A_{2xv} = \partial^3 A/\partial x^2 \partial V$. Thus, if the Helmholtz free energy and its derivatives are available (and these may be obtained by integrating and differentiating the P-V-T-x properties), then the two equations may be solved for any two of the three variables T_c, V_c, x_c. In the calculations presented here, the P-V-T-x relationships of mixtures were obtained from the (known) P-V-T properties of the reference substance (methane) and the extended corresponding states principle. Equations 6 and 7 were then solved for T_c and V_c at various values of x_c, thus yielding the critical locus. (P_c may be obtained using the corresponding states equations when T_c, V_c and x_c are known.)

Results of the calculations are shown in Figures 2–4. A single value of 0.89 for the binary interaction coefficient ξ_{12} was obtained from a "best fit" of the critical properties of the system. Figures 2–4 show that the fit to the data is better for mixtures rich in propane and becomes relatively worse for mixtures rich in perfluorocyclobutane. This is not unexpected, since the properties of propane may be predicted accurately from the properties of methane and the shape factor approach. This is not true for perfluorocyclobutane. Nevertheless the overall fit of the data (average absolute deviations of 0.8°K in critical temperature, 60 kPa in critical pressures and 0.001 $m^3\ kmol^{-1}$ in critical volumes) using a single value of the binary interaction coefficient (0.89) is considered very encouraging. This value of the binary interaction coefficient will be used to predict the one and two phase behavior of the system in subsequent papers of the series.

NOTATION

A = Helmholtz free energy
P = Pressure
T = Thermodynamic temperature
V = Volume
x = mole fraction
ξ = binary interaction coefficient

Subscript

1,2 = components 1, 2

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