Volumetric Properties of Supercritical Ethane-*n*-Heptane Mixtures: Molar Volumes and Partial Molar Volumes

Molar volumes were measured and partial molar volumes were calculated in the supercritical region, including the vicinity of the critical locus, for compositions of 1.8 to 20 mole % *n*-heptane. Molar volumes can be represented, to a reasonable approximation, by the Flory-Orwoll-Vrij (FOV) reduced equation of state. A better fit of the data is possible if the three exponents in the FOV equation are adjusted The modified FOV equation or the Redlich-Kwong equation, with parameters adjusted to fit the critical locus, can in general represent the partial molar volumes adequately along the critical locus only. The prediction of the composition-dependence of the partial molar volumes is only qualitatively successful at best.

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SCOPE

A good deal is known about gas-liquid equilibria of paraffin mixtures, and the location of the gas-liquid critical lines (critical locus) has been determined for many binary mixtures of this type (Kay, 1968). Little information, on the other hand, is available on their thermodynamic properties in the supercritical phase. Some of these properties, for example the negative partial molar volumes of mixtures containing polar components (Ehrlich and Fariss, 1969) and presumed to exist in binary paraffin mixtures with components of sufficient size difference as well, appear quite anomalous in the context of the behavior of liquid mixtures at low reduced temperatures.

The paraffin pair chosen represents two components of a most important homologous series which differ substantially in chain length. Any generalization of the results obtained in a study of the system ethane-*n*-heptane to mixtures in which the components exhibit varying molecular sizes and size differences is likely to be of interest in petroleum recovery and refining, as well as in the engineering of high pressure polyethylene processes. (The mixture ethane-polymethylene is a good model for ethylene-polyethylene.) Since, according to transition state theory, the pressure-coefficient of the reaction rate constant can be represented in terms of the compressibility of the mixture and the partial molar volumes of reactants and activated complex, a knowledge of the volumetric properties of supercritical systems should help in a solution of kinetic as well as thermodynamic problems.

Molar volumes of the mixture ethane-*n*-heptane were therefore measured in the supercritical region, including the vicinity of the critical locus, over a pressure, temperature, and composition range corresponding to nearly pure ethane to about 20 mole % heptane, and partial molar volumes were obtained by the analysis of volume-composition plots constructed from pressure-volume isotherms. The results were compared with two different sets of calculations based on equations of state.

CONCLUSIONS AND SIGNIFICANCE

Two approaches were found which were, in general, qualitatively successful in predicting the molar volumes and partial molar volumes in the region investigated. One of these was based on the reduced equation of state of Flory, Orwoll, and Vrij (FOV), used in conjunction with Prigogine's principle of corresponding states (PPCS) for chain molecule mixtures, the other on the Redlich-Kwong (RK) equation of state. The former method, in its original form, involves fewer arbitrary assumptions and can be extended in a straightforward manner to other binary mixtures of the same homologous series. The FOV equation was, however, proposed for liquids (negligible reduced pressure and low reduced temperature), and an empirical adjustment of its parameters was required for a good fit of the experimental data. The RK equation, on the other hand, requires knowledge of the critical locus before it can be used to calculate partial molar volumes by the present technique.

With the proper calibrations, the two approaches are qualitatively successful in predicting the partial molar volumes at the critical locus, except as the critical point of pure ethane is approached. Both approaches predict minima in the partial molar volume of *n*-heptane plotted versus composition along the critical isotherms and isobars of any one of the mixtures investigated. The predicted minima deepen and sharpen as the critical composition is lowered toward pure ethane. Such minima probably exist, but they do not occur at the compositions predicted. It is likely that either of the two methods discussed is capable of extension to other paraffin mixtures to reproduce qualitatively their molar volumes and partial molar volumes in the supercritical region. Special problems, as yet unresolved, exist at low concentrations

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of the high molecular weight component, particularly near the critical point of the low molecular weight component.

The partial molar volumes of n-heptane are negative throughout the entire pressure, temperature, and composition range investigated in this study, and the excess volumes are also negative. Calculations of reaction rate constants must take these large nonidealities into account.

The region in temperature T, pressure P, and composition x space chosen for the determination of the volumetric properties[*] of the binary paraffin mixture ethane-n-heptane included the 1-phase (supercritical) region immediately adjoining the ascending branch of the critical locus, that is, the part representing compositions between nearly pure ethane and that corresponding to the pressure maximum ($x = 0.23$). The critical locus of the mixture is shown in Figure 1. The region investigated extended over a small interval in temperature ($\Delta T = T - T_c$) and pressure ($\Delta P = P - P_c$), near the critical values corresponding to a given composition, but ranged over wider values of x, sometimes between about 0.018 and 0.20. The measurements were therefore carried out over parallelepipeds in P, T, x space, with x as the major dimension, one parallelepiped for each of six critical points. The slope of the critical locus $(dP/dT)_c$ is positive in the region investigated.

EXPERIMENT (WU, 1972)

Measurements were carried out in a variable-volume equilibrium vessel immersed in an oil thermostat (Figure 2). The vessel consisted of two arms into which the components were introduced, initially separated by mercury. The vessel fulfilled three functions: mixing of the components, separation of the pump oil from the experimental mixture, and provision of a visible (oil-mercury) meniscus whose displacement allowed calculation of volume changes. The presence of the two separate arms in the equilibrium vessel allowed a measurement of the volume change of mixing. In the experiments to be reported here, however, $\bar{v}_1$ and $\bar{v}_2$ were calculated directly from plots of the molar volume as a function of composition, obtained from the P-V isotherms.

The volume of the equilibrium vessel (partly filled with mercury) was 363 cc; the sensitivity of the two different Jerguson gauges used in this work were 1.90 and 3.75 cc/cm, respectively; pressure could be measured to ± 0.5 lb./sq.in., and temperature was measured and held constant to ± 0.05°C. The total volume of the mixture could be obtained with a maximum error of ± 1.6%. The error in the calculation of the partial molar volume is discussed in the text.

The components of the mixture were obtained from Phillips Petroleum. The ethane (Pure Grade) was stated to be 99.35% pure, the n-heptane (Research Grade) 99.92%.

RESULTS

Molar Volumes

The P-V isotherms and many of the original calculations are collected in a separate reference (Wu, 1972). Figure 3 shows typical $V(x)$ isotherms at two different pressures, one of which contains a critical point.[†]

A representation of the molar volume at all compositions, temperatures, and pressures by means of a single plot should be possible, if the corresponding states principle applies, together with a reduced equation of state which is adequate at the experimental temperatures and pressures. An equation of state in reduced variables which satisfies pure hydrocarbons, as well as polymer solutions at normal temperatures and pressures, and which has a foundation in statistical mechanics, is that of Flory, Orwoll and Vrij (FOV) (Flory, 1964). Although the equation was originally proposed for use with liquids, it is useful to explore its use with our data and to modify it empirically.

The FOV equation can be written as

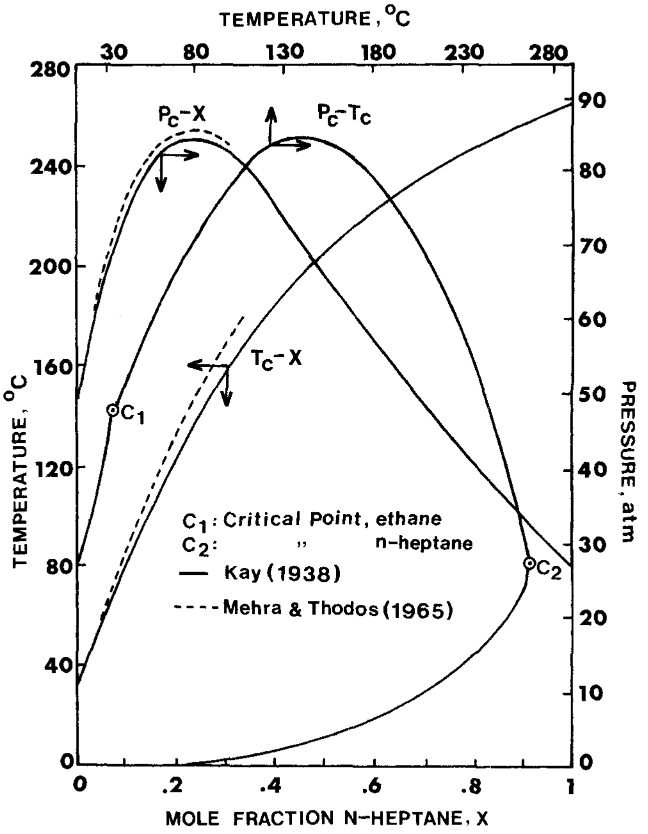

Fig. 1. Critical locus of ethane-n-heptane.

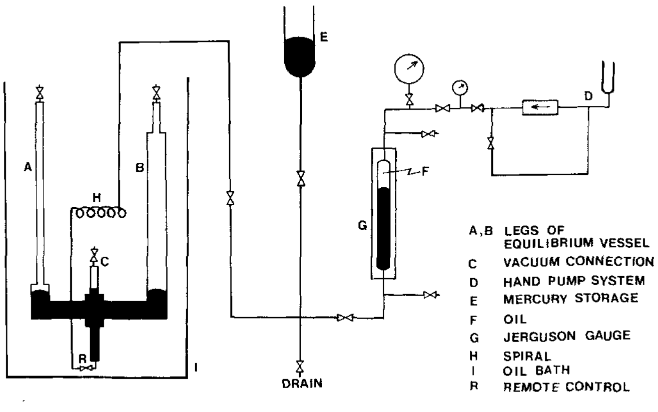

Fig. 2. Experimental arrangement.

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[*] See also the following paper.

[†] The data are consistent with the possibility that $(\partial^2V/\partial x^2)_T$ may vanish at the critical point (W. J. Gaw and R. L. Scott, *J. Chem. Thermo.*, 3, 335 (1971).

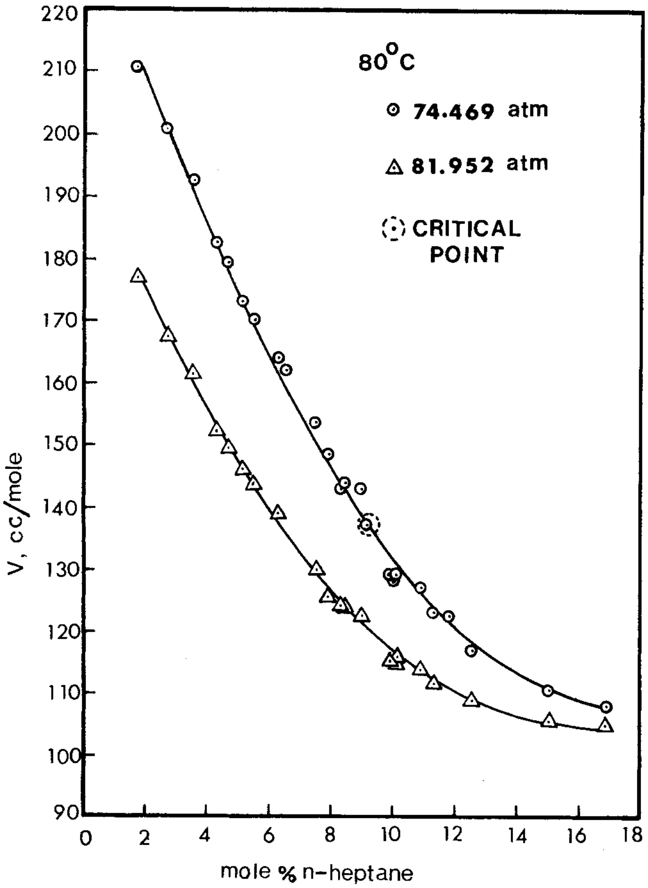

Fig. 3. Molar volume vs. composition.

Table 1. Reference Parameters for FOV Equation

	P^*, atm	V^*, cc/mole	T^*, °K
Ethane	3218	43.04	2674
n-Heptane	4223	113.74	4671

$$\tilde{T} = (\tilde{P}\tilde{V}^{k_1} + 1/\tilde{V}^{k_2})(1 - 1/\tilde{V}^{k_3}) \qquad (1)$$

where all reduced quantities (~) are defined with respect to reference parameters (*) which can be obtained by examination of the *P-V-T* behavior of the pure components. The exponents k_1, k_2, and k_3 are equal to 1, 1, and 1/3 respectively. The reference pressure P^* is given by U^*/V^* where U^* is the intermolecular reference energy.

Prigogine's formulation of the principle of corresponding states (PPCS) allowed its extension to chain molecules and chain molecule mixtures and the specification of self-consistent reference parameters for members of a homologous series (Prigogine, 1957). Patterson and Delmas (1969) recommended a set of reference parameters for alkanes to be used with PPCS based on considerations put forward by Flory and collaborators (Flory, 1964; Orwoll, 1967). The parameters for ethane and *n*-heptane are listed in Table 1.

The properties of the mixture can be calculated from the data for the pure components by the assumption that the reference volume V^* and energy U^* may be computed as mole fraction averages, and the reduced temperature $\tilde{T}$ as segment fraction (ϕ) average (Patterson, 1969).

The molar volume data plotted according to the FOV equation are shown in Figure 4. The fit, as anticipated, is not particularly good but much improved by adjustment of the exponents according to a nonlinear least squares optimization technique (Figure 4). When the exponents are adjusted individually for data taken along different isotherms and isobars a substantial variation in their magnitudes is found. The adjusted values of Figure 4 represent an average weighted according to the number of points along individual isotherms and isobars. A similar empirical adjustment of exponents is practiced with the Yang-Yendall equation (Yang and Yendall, 1971).

$$\tilde{P} = \frac{\tilde{T}}{\tilde{V} - \tilde{V}^m} - \frac{1}{\tilde{V}^n} \qquad (2)$$

which reduces to the FOV equation when m = 2/3 and n = 2. An estimate of the molar volume according to the FOV equation would evidently have been a useful first approximation.

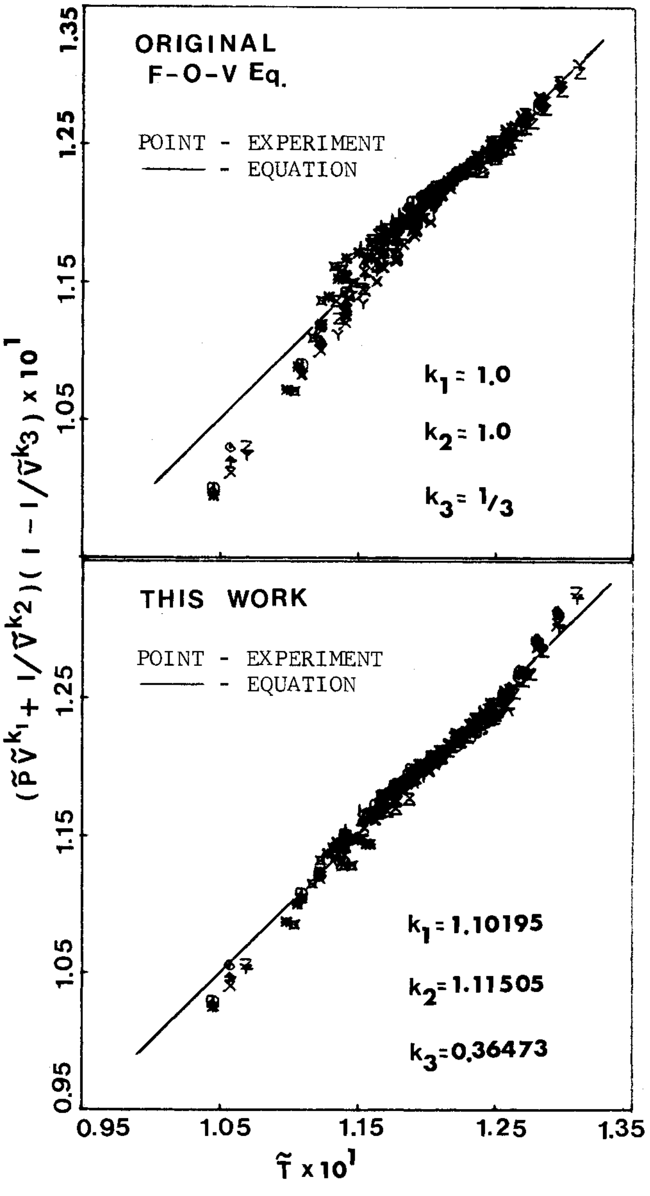

Fig. 4. Molar volume plotted according to the FOV equation in its original form and with its exponents adjusted.

Partial Molar Volumes

To calculate the partial molar volumes $\overline{v}_1(x)$ and $\overline{v}_2(x)$ from the experimental data of $V(x)$, the latter are fitted with polynomials of order three and four. The partial molar volumes are then calculated from the equations

$$\overline{v}_1 = V - x_2(\partial V/\partial x_2)_{T,P}, \quad \overline{v}_2 = V - x_1(\partial V/\partial x_1)_{T,P} \qquad (3)$$

The results of applying this procedure to the data plotted in Figure 3 are shown in Table 2 and Figure 5.

The results from the polynomials of different order are similar in the interior of the curve but diverge near the ends. Use of polynomials of order higher than four is not justified, since these do not, in general, improve the fit and tend to introduce spurious oscillations, whereas a minimum order of three is required by the possible presence of a point of inflection in $V(x)$ and extrema in $\overline{v}(x)$. The calculation of the partial molar volumes is, in general, satisfactory, but uncertainties exist near the ends of the curves. Figures 6, 7, and 8 show plots of $\overline{v}(x)$ for both components, each containing a critical point. Note the possible presence of minima in $\overline{v}_2(x)$ at low heptane contents. The partial molar volumes of *n*-heptane are negative throughout the region investigated and so are the excess volumes.

The experimental data are to be compared with calculations made according to the modified FOV and RK equations. The partial molar volumes are calculated with the help of the equation

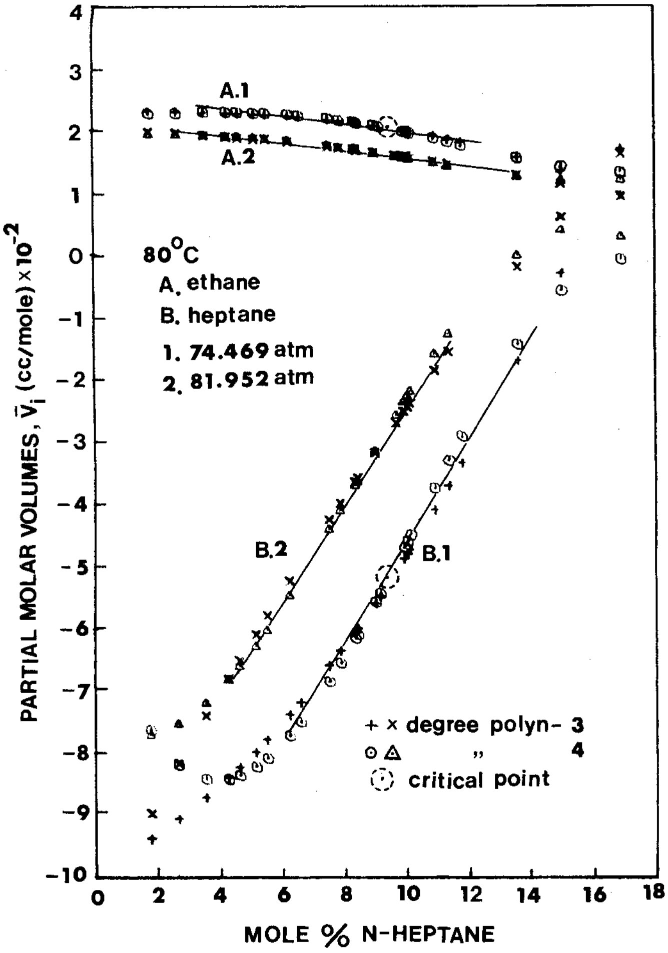

Fig. 5. Partial molar volumes plotted according to polynomial analyses.

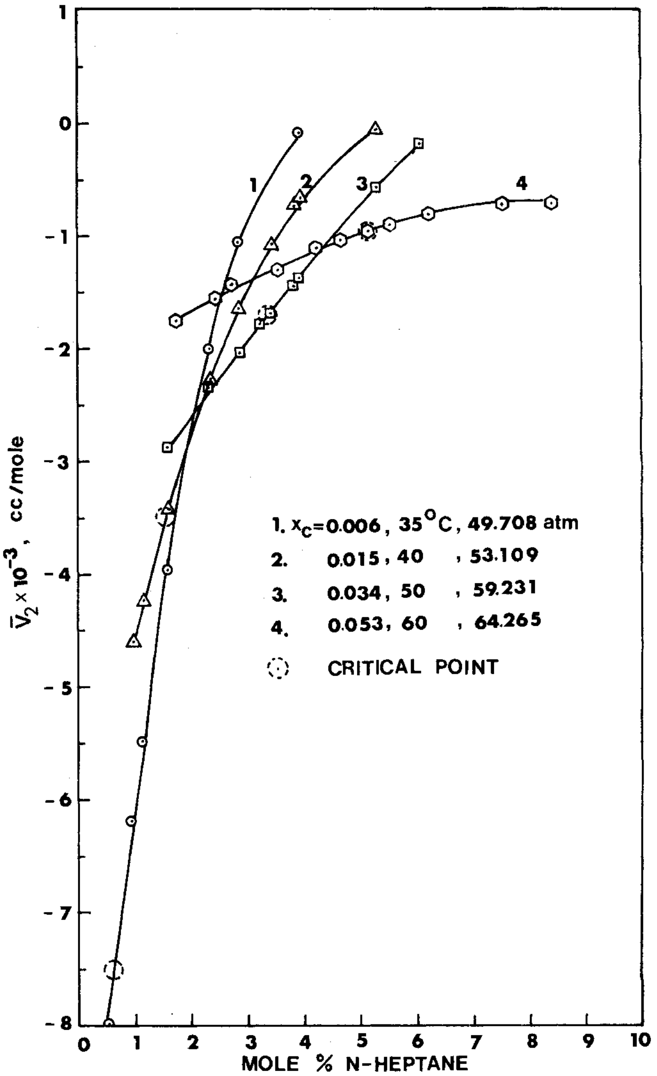

Fig. 6. Partial molar volumes of *n*-heptane vs. composition.

$$\overline{v}_2 = -\frac{(\partial P/\partial n_2)_{T,V_t,n_1}}{(\partial P/\partial V_t)_{T,n_1,n_2}} \qquad (4)$$

According to the FOV equation, the numerator and denominator in Equation (4) are given by

$$\begin{aligned}(\partial P/\partial n_2)_{T,V_t,n_1} = {} & (1/n_t)\,\{(C_4/C_5)(P^*\,\tilde{V}) \\ & + x_1\tilde{P}(dP^*/dx_2) + (C_4/C_5)(P^*\,\tilde{V}/V^*)x_1(dV^*/dx_2) \\ & - (1/C_5)(P^*\,\tilde{T}/T^*)\,[r/(x_1 + x_2 r)^2]\,x_1(dT^*/d\phi_2)\}\end{aligned} \qquad (5)$$

and by

$$(\partial P/\partial V_t)_{T,n_1,n_2} = -\,(1/n_t)(C_4/C_5)(P^*/V^*) \qquad (6)$$

with similar expressions for $\overline{v}_1$ and $(\partial P/\partial n_1)_{T,V_t,n_2}$
The five constants C_i are given by

$$\begin{aligned} & C_1 = \tilde{P}\tilde{V}^{k_1} + 1/\tilde{V}^{k_2}, \quad C_2 = 1 - 1/\tilde{V}^{k_3}, \\ & C_3 = \tilde{P}k_1\tilde{V}^{k_1-1} - k_2(1/\tilde{V}^{k_2+1}), \\ & C_4 = C_2C_3 + k_3C_1(1/\tilde{V}^{k_3+1}), \quad C_5 = C_2\tilde{V}^{k_1} \end{aligned} \qquad (7)$$

and $r = r_2/r_1$, $r_1 = s_1 + 1$, with s_1 given by the number

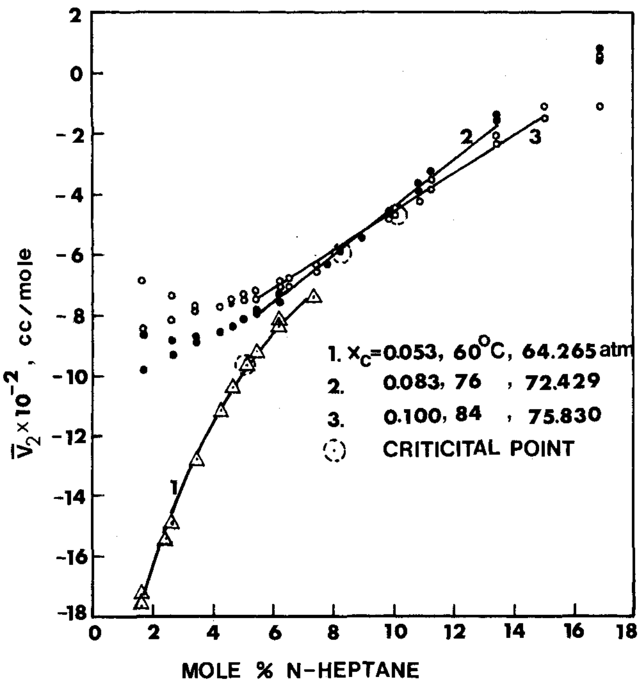

Fig. 7. Partial molar volumes of *n*-heptane vs. composition.

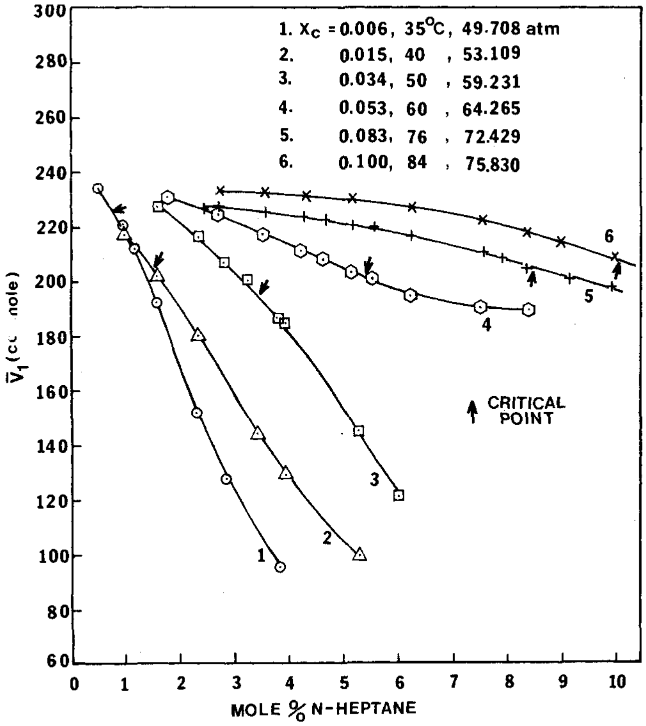

Fig. 8. Partial molar volumes of ethane vs. composition.

of carbon atoms of component 1. Alternatively, $\overline{v}_1$ and $\overline{v}_2$ may be calculated from

$$(\partial V/\partial x_2)_{T,p} = (C_5/C_4)\, V^*(\tilde{P}/P^*)\,(dP^*/dx_2) + \tilde{V}\,(dV^*/dx_2) - (1/C_4)\,(V^*\,\tilde{T}/T^*)\,[r/(x_1 + x_2 r)^2]\;(dT^*/d\phi_2) \qquad (8)$$

followed by Equation (3).

According to the RK equation,

$$P = \frac{RT}{V - b} - \frac{a}{T^{1/2}V(V + b)} \qquad (9)$$

and the derivatives required to calculate $\overline{v}$ are given by

$$(\partial P/\partial n_i)_{T,V_t,n_{j(j\neq i)}} = \frac{1}{n_t}\left\{\left(\frac{RT}{V - b}\right)\left(1 + \frac{b_i}{V - b}\right) - \frac{2(\sum_j x_j a_{ij}) - ab_i/(V + b)}{T^{1/2}V(V + b)}\right\} \qquad (10)$$

TABLE 2. EXPERIMENTAL MOLAR VOLUME AND CALCULATED PARTIAL MOLAR VOLUMES AT 80.0°C AND 74.47 ATM

Mole fraction Heptane	Exptl Volume cc/mol	Partial molar volumes, cc/mole Polynomial = 3 Ethane	Heptane	Polynomial = 4 Ethane	Heptane
.018	210.5	232.1	−937.5	227.7	−761.5
.027	200.5	231.4	−906.6	228.9	−817.3
.036	192.5	230.2	−871.7	229.7	−841.7
.043	182.5	228.9	−839.6	229.7	−842.2
.046	179.0	228.1	−822.9	229.5	−836.8
.052	173.0	226.8	−797.4	228.8	−822.9
.055	170.0	225.7	−777.9	228.0	−808.7
.063	164.0	223.2	−737.2	225.6	−771.8
.066	162.0	221.8	−717.2	224.2	−750.9
.075	153.5	217.3	−658.6	219.1	−683.3
.079	148.5	215.4	−634.9	216.6	−654.2
.083	143.0	212.6	−603.6	213.1	−614.9
.084	144.0	212.1	−598.1	212.5	−607.9
.090	143.0	208.2	−557.5	207.6	−556.3
.092	137.0	207.0	−545.8	206.1	−541.5
.099	129.0	200.8	−486.9	198.3	−467.6
.100	128.0	199.9	−478.3	197.1	−457.1
.101	129.0	199.1	−471.2	196.2	−448.4
.109	127.0	191.7	−408.4	187.4	−373.8
.114	123.0	186.9	−370.0	181.9	−330.5
.118	122.5	182.0	−333.1	176.8	−291.0
.136	117.0	158.4	−170.9	155.5	−144.6
.150	110.5	134.8	−30.0	141.2	−58.3
.169	108.0	96.8	170.1	131.8	−8.2

Avg. abs. % error in fitting of molar volume are: Polynomial of Degree 3 = 1.007; Polynomial of Degree 4 = 0.953.

TABLE 3. PROPERTIES OF PURE COMPONENTS AND PARAMETERS USED WITH RK EQUATIONS (CHUEH-PRAUSNITZ)

T_{c1} (°K)	T_{c2} (°K)	P_{c1} (atm)	P_{c2} (atm)	V_{c1} (l mole^{-1})	V_{c2} (l mole^{-1})
305.5	540.2	48.2	27.0	0.148	0.426

a_{11}	a_{22}	a_{12}	b_1	b_2	Ω_{a1}	Ω_{a2}	Ω_{b1}	Ω_{b2}
96.57	706.1	279.6	4.47×10^{-2}	1.374×10^{-1}	0.424	0.417	0.0855	0.0837

ω_1	ω_2	k_{12}	$2\tau_{12}/(T_{c1} + T_{c2})$	$2\upsilon_{12}/(V_{c1} + V_{c2})$
0.105	0.349	0.04	0.0743	−0.683

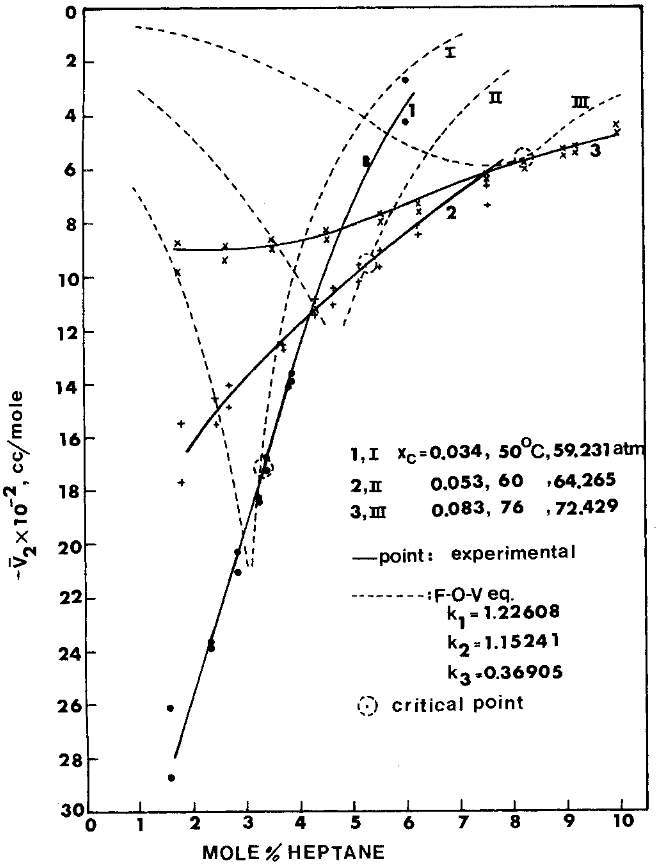

Fig. 9. Experimental partial molar volumes of *n*-heptane compared with values calculated from the FOV equation.

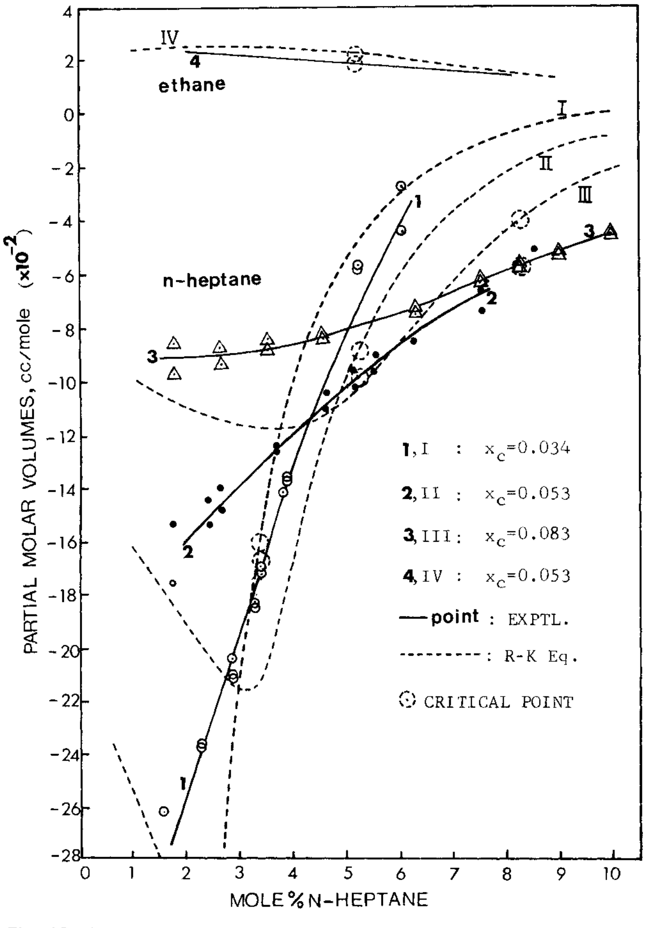

Fig. 10. Experimental partial molar volumes of ethane and *n*-heptane compared with values calculated from the RK equation.

$$(\partial P/\partial V_t)_{T,n_j(\text{all } j)} = \frac{1}{n_t}\left\{ \frac{-RT}{(V-b)^2} + \frac{a(2V+b)}{T^{1/2}V^2(V+b)^2} \right\} \quad (11)$$

In order to obtain *V*, a cubic equation is solved by an iterative technique.

The parameters *a* and *b* for the pure components are calculated from the critical data (Reid and Sherwood, 1966) according to the method of Chueh and Prausnitz; the same authors' combining rules and adjustment factors were used to calculate the equation of state parameters, critical temperatures, and volumes of the mixtures (Chueh and Prausnitz, 1967; Prausnitz, 1969). The values of the parameters required are listed in Table 3.

The experimental data along several of the isotherms and isobars intersecting the critical locus are now compared with the results obtained from the modified FOV equation (Figure 9) and the RK equation (Figure 10). The experimental and calculated points are seen to match at the critical point in the former case. This was accomplished by forcing agreement of the critical partial molar volumes by means of a nonlinear least squares optimization technique similar to that used to fit the molar volumes. Optimum fit of the partial molar volume data

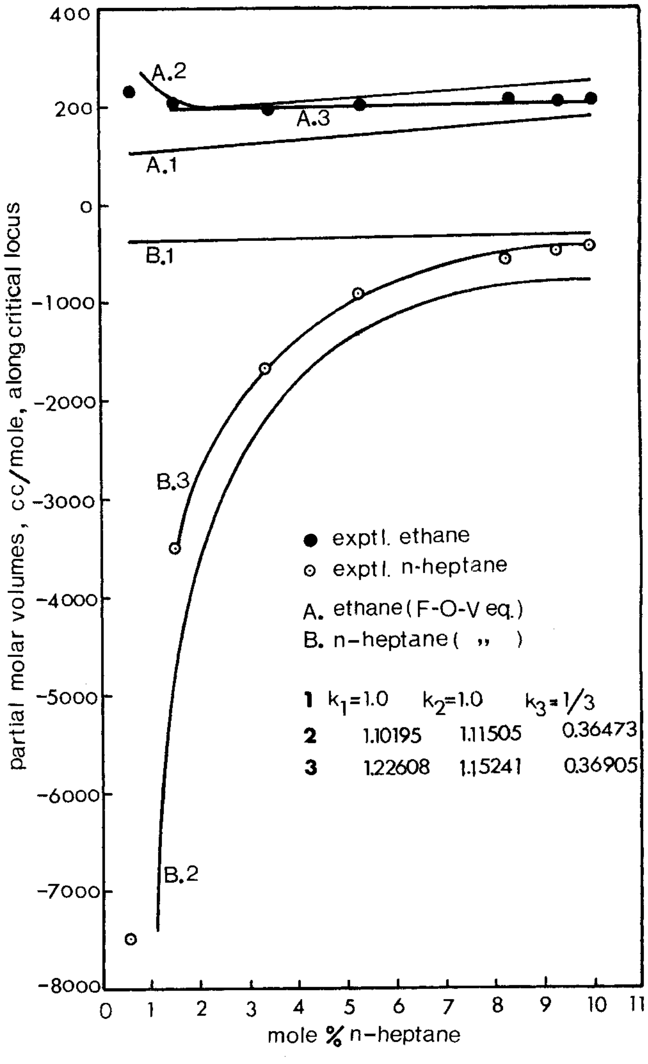

Fig. 11. Experimental and FOV partial molar volumes along the critical locus. K_1, k_2, k_3 chosen for best fit of the molar volume—curves 2; of the partial molar volumes—curves 3.

requires somewhat different exponents (Figure 9) than optimum fit of the molar volume data (Figure 4). The close agreement between the experimental critical partial molar volumes and those calculated from the RK equation (Figure 10) are not unexpected since the methods of Chueh and Prausnitz (1967, 1969) had been used to assure a good fit of the *P-V-T* data along the critical locus.

The agreement between experimental and calculated values away from the critical locus is much poorer according to either type of calculation. Note that either method predicts well defined minima in $\bar{v}_2(x)$ which deepen and move to compositions lower in heptane along isotherms and isobars which are critical for increasingly lower heptane concentrations. The experimental data do not clearly establish the presence of such minima, and if they do exist, they occur at heptane concentrations lower than predicted. It is likely that the relative magnitude and shift in the minima predicted by the two types of calculation is correct, and this appears to be consistent with predictions from the decorated lattice-gas model (Wheeler, 1972). The form of $\bar{v}_2$ along the critical locus is extremely sensitive to the magnitude of the exponents in the modified FOV equation (Figure 11). That equation and the RK equation are capable of a good representation of $\bar{v}_1$ and $\bar{v}_2$ along the critical locus when properly calibrated (Figures 11, 12). Note that $\bar{v}_2$ becomes highly negative as the critical point of ethane is approached. The decorated lattice-gas model predicts infinities for both $\bar{v}_1$ and $\bar{v}_2$ at that point (Wheeler, 1972).

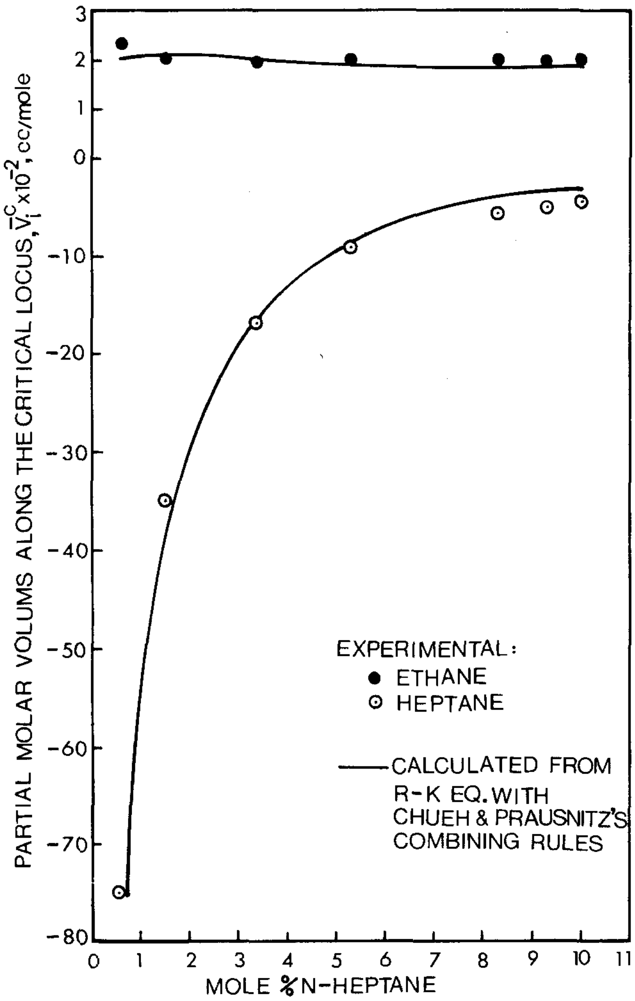

Fig. 12. Experimental and RK partial molar volumes along the critical locus.

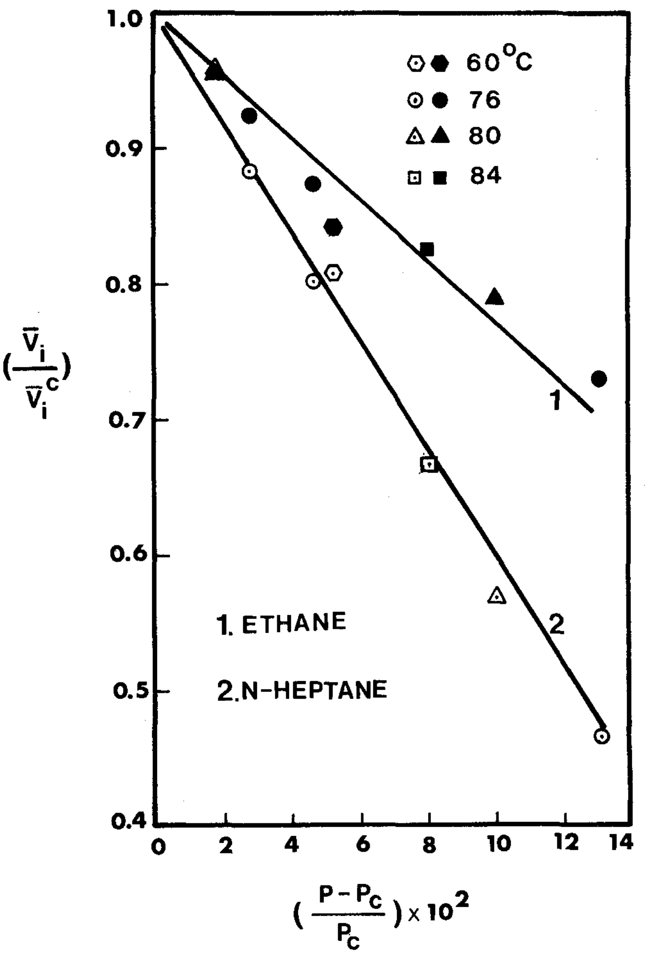

Fig. 13. Reduced partial molar volumes as a function of distance from the critical locus along the pressure coordinate.

In the rather narrow region of supercritical space investigated, empirical correlations for v_1 and v_2 can be established along reduced variable coordinates (Figure 13).

DISCUSSION

It is probable that, by measurements carried out closer to the critical point of the lower molecular weight component and extended to paraffin mixtures whose members exhibit a greater difference in chain length, the volumetric properties of this important class of mixtures can be mapped by methods similar to those employed here. Such information should not only be important for the engineering of nonreacting supercritical mixtures but also in reaction engineering. The high pressure polyethylene process, for example, involves a highly nonideal supercritical hydrocarbon mixture and application of transition-state theory requires knowledge of the partial molar volumes (Ehrlich, 1971).

ACKNOWLEDGMENT

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NOTATION

T = temperature
P = pressure
x = mole fraction

V = molar volume
V_t = volume of sample
U^* = intermolecular reference energy
n_1 = moles of ethane
n_2 = moles of n-heptane
n_t = total number of moles
$\bar{v}_1$ = partial molar volume of ethane
$\bar{v}_2$ = partial molar volume of n-heptane
k_1, k_2, k_3 = exponents in FOV equation
n, m = exponents in Yang-Yendall equation
$a, b, a_{11}, a_{22}, a_{12}, b_1, b_2, \Omega_{a1}, \Omega_{a2}, \Omega_{b1}, \Omega_{b2}, k_{12}$ = constants in RK equation (Chueh and Prausnitz, 1967); a, b refer to average for mixture, except in Equation (9)
τ_{12} = adjustment parameter for critical temperature of mixture (Chueh-Prausnitz)
v_{12} = adjustment parameter for critical volume of mixture (Chueh-Prausnitz)
ϕ_2 = segment fraction of n-heptane $= x_2r/(x_1 + x_2r)$
s_1, s_2 = number of carbon atoms of components 1, 2
r_1 $= s_1 + 1, r_2 = s_2 + 1, r = r_2/r_1$
ω_1, ω_2 = acentric factors of components 1, 2
Superscript* = reference parameter
Superscript $\sim$ = reduced parameter
Subscripts c_1, c_2 = critical parameters of pure components

LITERATURE CITED

Chueh, P. L., and J. M. Prausnitz, "Vapor-Liquid Equilibria at High Pressures," *AIChE J.*, **13**, 1099, 1107 (1967).

Ehrlich, P., "Partial Molar Volume Anomaly in Supercritical Mixtures and the Free Radical Polymerization Ethylene," *J. Macromol. Sci.*, **A5**, 1259 (1971).

———., and R. H. Fariss, "Negative Partial Molar Volumes in The Critical Region: Mixtures of Ethylene and Vinyl Chloride," *J. Phys. Chem.*, **73**, 1164, 4433 (1969).

Flory, P. J., R. A. Orwoll, and A. Vrij, "Statistical Thermodynamics of Chain Molecule Liquids I. An Equation of State for Normal Paraffin Hydrocarbonds," *J. Am. Chem. Soc.*, **86**, 3507 (1964); II "Liquid Mixtures of Normal Paraffin Hydrocarbons," *ibid.*, **86**, 3515 (1964).

Kay, W. B., "Liquid-Vapor Phase Equilibrium Relations in Ethane-n-Heptane Systems," *Ind. Eng. Chem.*, **30**, 459 (1938).

———., "The Critical Locus Curve and the Phase Behavior of Mixtures," *Accounts Chem. Res.*, **1**, 344 (1968).

Mehra, V. S., and G. Thodos, "Vapor-Liquid Equilibrium in the Ethane-n-Heptane System," *J. Chem. Eng. Data*, **10**, 211 (1965).

Orwoll, R. A., and P. J. Flory, "Equation of State Parameters for Normal Alkanes. Correlation With Chain Length," *J. Am. Chem. Soc.*, **89**, 6814 (1967).

Patterson, D., and G. Delmas, "Critical State in Chain-Molecule Mixtures," *Trans. Faraday Soc.*, **65**, 708 (1969).

Prausnitz, J. M., *Molecular Thermodynamics of Fluid Phase Equilibria*, App. VIII, Prentice Hall, Englewood Cliffs, N. J. (1969).

Prigogine, I., *The Molecular Theory of Solutions*, Chapt. 16, North-Holland, Amsterdam (1957).

Reid, R. C., and T. K. Sherwood, *The Properties of Gases and Liquids*, McGraw-Hill, 2nd ed. (1966).

Wheeler, J. C., "Behavior of a Solute Near the Critical Point of an Almost Pure Solvent," *Ber. d. Bunsenges, f. phys. chem.*, **76**, 308 (1972).

Wu, P. C., "Volumetric Properties of Ethane-n-Heptane Mixtures in the Supercritical Region," dissertation, State Univ. New York, Buffalo (1972).

Yang, C. L., and E. F. Yendall, "Equation of State for Phase Equilibrium," *AIChE J.*, **17**, 596 (1971).

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Volumetric Properties of Supercritical Ethane- *n* -Heptane Mixtures: The Isothermal Compressibility in the Critical Region

The isothermal compressibility (at constant composition x) $k_{T,x}$, was calculated in the neighborhood of the critical locus for seven mixtures containing 3.5 to 19.6 mole % heptane and analyzed in terms of the reduced pressure variable $\sigma = (P - \hat{P})/\hat{P}$ where $\hat{P}$ is the pressure at which $k_{T,x}$ becomes very large. The data can be represented by the equation $k_{T,x} =$ const. $\sigma^{-\lambda}$ along the critical isotherm and one near it and by the locus $\hat{P}(T)$. λ was found to be a strong function of x. The divergence of the isothermal compressibility of the mixtures near the critical locus is in conflict with predictions from classical equations of state but in accordance with modern concepts of the critical region.

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According to empirical equations of state, of which the van der Waals equation is the prototype, the isothermal compressibility displays a simple infinity at the critical point of a pure fluid but is finite at the critical point of a mixture. According to modern concepts, however, whether based on general thermodynamic arguments which reject the postulate that the Helmholtz free energy is an analyti-

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