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

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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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SCOPE

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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cal function of temperature and volume near the critical point or on specific statistical models, the compressibility of a mixture diverges at the critical point (Fisher, 1967; Rowlinson, 1969).

It was the objective of this investigation to measure the isothermal compressibility as the critical point was approached from the one-phase (supercritical) region in ethane-*n*-heptane mixtures for compositions ranging from about 3.5 mole % heptane to about 20 mole % heptane. It was found convenient to make the approach along the pressure axis.

The data supplement the thermodynamic description of the critical region of this mixture which also formed the subject of the previous paper (Wu and Ehrlich, 1973). Results are discussed in terms of the classical and modern points of view.

CONCLUSIONS AND SIGNIFICANCE

The divergence of the isothermal compressibility $k_{T,x}$ along the pressure axis found experimentally and described by the equation $k_{T,x} = A\sigma^{-\lambda}$ is inconsistent with the convergence of that variable in mixtures according to the classical point of view. (A is a constant, $\sigma = (P - \hat{P})/\hat{P}$, $\hat{P}$ is the pressure at which $k_{T,x}$ becomes very large, $\hat{P} = P_c$ at $\theta = 0$, where $\theta = (T - T_c)/T_c$ and the subscript c refers to the critical value). The introduction of the variable $\hat{P}$ allows the specification of a locus of states of maximum compressibility in T-V-P space terminating at the critical point for each composition, and the magnitude of the compressibility at small but finite values of σ is determined by A, σ and θ. λ is found to be a function of x.

Magnitudes of the parameters calculated from experiment are discussed in terms of classical and modern concepts. The specification of the isothermal compressibility in terms of the reduced variables σ and θ appears to be useful in a region close to the critical locus where classical equations of state exhibit their inconsistencies and are apt to be grossly in error in estimating $k_{T,x}$ and where modern theories are as yet unable to provide numerical estimates of that variable.

It was the objective of this study to determine the isothermal compressibility $k_{T,x}$ in the supercritical region near the critical locus where predictions of its magnitude according to the equation of state were likely to prove inadequate. The calculations could be performed by analyzing some of the *P-V* isotherms collected to determine molar volumes and partial molar volumes in the supercritical region (Wu and Ehrlich, 1973).

A possible choice of independent variable was the pressure, and it was of obvious interest to study the approach of $k_{T,x}$ to a finite value, or its divergence, not only along the critical isotherm but also one near it. Figure 1 shows the phase behavior near the critical point. (For further details, see Kay, 1968). $k_{T,x}$ was calculated from the *P-V* isotherms obtained upon compression of all

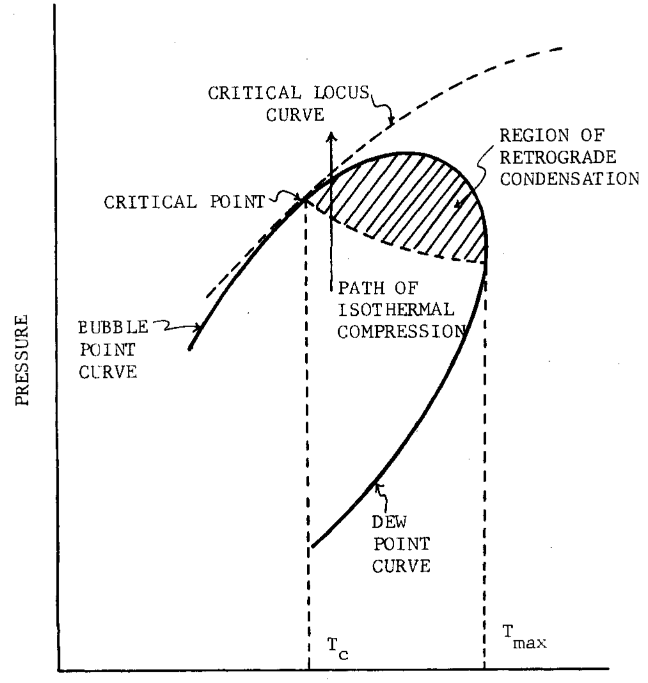

Fig. 1. Path of isothermal compression.

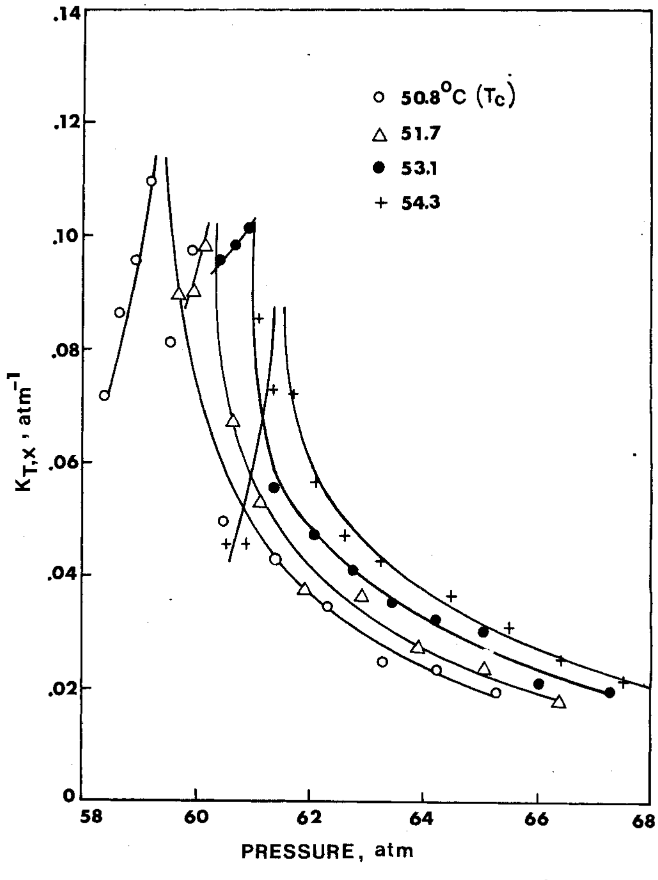

Fig. 2. Isothermal compressibility $k_{T,x}$ vs. pressure for a mixture containing 3.47 mole % *n*-heptane.

mixtures from the 2-phase into the 1-phase (supercritical) region.

EXPERIMENT

The equipment was that described in Wu and Ehrlich (1973). Because of the large effect of pressure on $k_{T,x}$ in the critical region, the equilibrium vessel was kept in a near-horizontal position during measurement to eliminate, or at least minimize, any pressure gradient in it.

RESULTS

A typical plot of $k_{T,x}$ versus pressure is shown in Figure 2. The general character of the plots does not change with temperature. $k_{T,x}$ diverges, but the location of the singularity along the pressure axis is rather well defined. Some instability was observed on the low-pressure side of the maximum, and only the high-pressure sides of the curves, which lie in the supercritical region, were analyzed. The critical temperature could not be found independently by the present method and was located according to the experimental data of Kay (1938) and Mehra and Thodos (1965). An inspection of Figure 2 indicates, and the analysis of the data confirms, that neither the pressure-dependence nor the numerical specification of $k_{T,x}$ requires an accurate knowledge of the critical temperature T_c.

To analyze the behavior of $k_{T,x}$ we choose as independent variable the reduced quantity, $\sigma = (P-\hat{P})/\hat{P}$, where

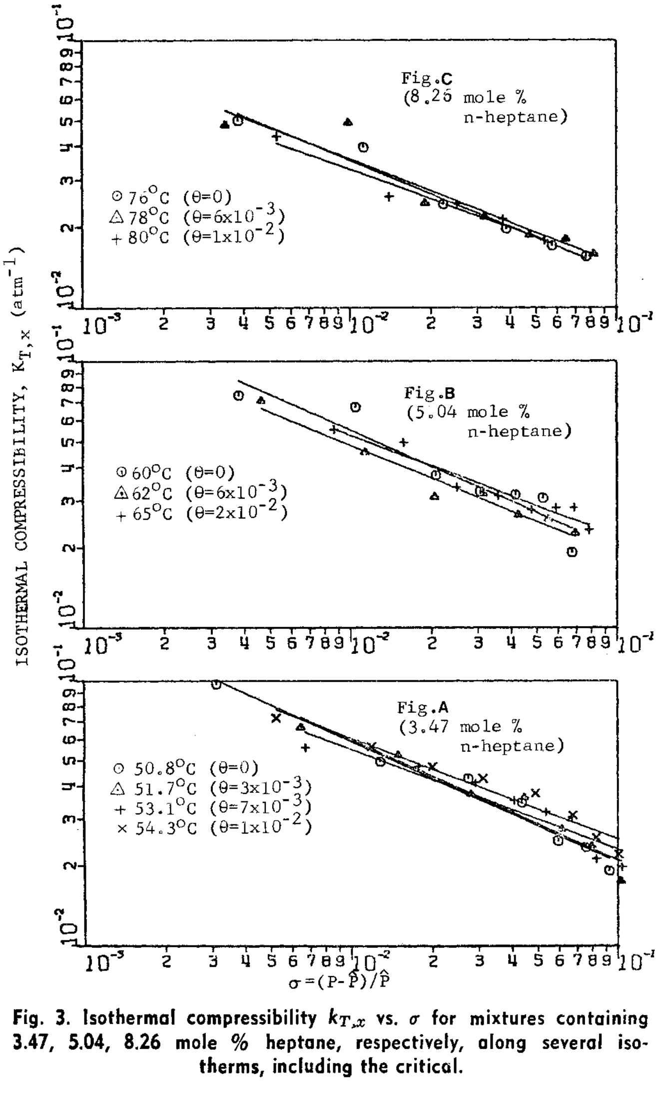

Fig. 3. Isothermal compressibility $k_{T,x}$ vs. σ for mixtures containing 3.47, 5.04, 8.26 mole % heptane, respectively, along several isotherms, including the critical.

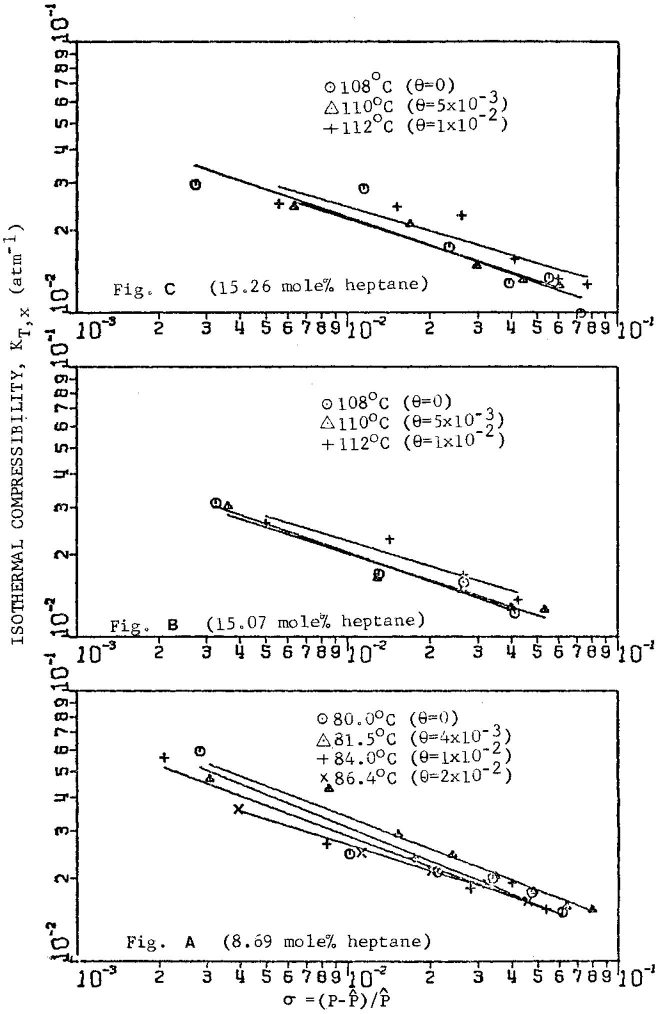

Fig. 4. Isothermal compressibility $k_{T,x}$ vs. σ for mixtures containing 8.69, 15.07 and 15.26 mole % heptane, respectively, along several isotherms, including the critical.

where $\hat{P}$ is the pressure at which plots like Figure 2 shows a singularity of $k_{T,x}$. Figures 3 and 4 are plots of log $k_{T,x}$ versus log σ along several isotherms, slightly above and including the critical one, for mixtures in the range of 3.47 to 15.26 mole % heptane. When these data are considered together, no justification for drawing other than linear plots exists, although when some of the plots are examined individually that conclusion is not always justified. All plots in Figures 3 and 4 have been drawn by computer as straight lines according to a least squares analysis and may be represented by the equation

$$\log k_{T,x} = \log A - \lambda \log (\sigma/\sigma_0)$$

$$2 \times 10^{-3} < \sigma \leq 10^{-1} \qquad (1)$$

where A is the value of $k_{T,x}$ at the arbitrary reduced reference pressure of $\sigma_0 = 0.1$. Since σ denotes distance from the critical point (or the point of maximum compressibility) along the pressure-axis, it is appropriate to introduce another reduced variable, $\theta = (T - T_c)/T_c$ which defines distance from the critical isotherm.

The results of this analysis are summarized in Table 1. Note the relative insensitivity of $k_{T,x}$ to temperature in contrast to what is observed in pure fluids and the decrease of λ with x (Figure 5, Table 1).* The empirical descrip-

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* A also decreases with λ (Figure 6) and this implies that at a fixed distance from the critical locus (σ, θ constant) the compressibility decreases with heptane content along the ascending branch of the critical locus.

TABLE 1. THE PARAMETERS λ AND A OF EQUATION (1)

Mole % heptane	Temp., °C	$\theta = \frac{T - T_c}{T_c}$	Index λ	A, atm^{-1}
3.47	50.8	0	0.48(±0.09)	0.0207(±0.0007)
	51.7	3×10^{-3}	0.44(0.03)	0.0213(0.0002)
	53.1	7×10^{-3}	0.37(0.05)	0.0233(0.0002)
	54.3	1×10^{-2}	0.36(0.04)	0.0255(0.0004)
5.04	60.0	0	0.43(0.07)	0.0202(0.0011)
	62.0	6×10^{-3}	0.37(0.07)	0.0195(0.0009)
	65.0	2×10^{-2}	0.35(0.07)	0.0224(0.0003)
8.26	76.0	0	0.38(0.08)	0.0140(0.0008)
	78.0	6×10^{-3}	0.36(0.06)	0.0149(0.0006)
	80.0	1×10^{-2}	0.33(0.07)	0.0147(0.0008)
8.69	80.0	0	0.36(0.11)	0.0127(0.0014)
	81.5	4×10^{-3}	0.36(0.09)	0.0143(0.0010)
	84.0	1×10^{-2}	0.35(0.10)	0.0126(0.0014)
	86.4	2×10^{-2}	0.28(0.07)	0.0136(0.0010)
15.07	108.0	0	0.32(0.05)	0.0094(0.0004)
	110.0	5×10^{-3}	0.30(0.06)	0.0098(0.0004)
	112.0	1×10^{-2}	0.25(0.07)	0.0118(0.0009)
15.26	108.0	0	0.31(0.06)	0.0105(0.0005)
	110.0	5×10^{-3}	0.28(0.07)	0.0108(0.0006)
	112.0	1×10^{-2}	0.20(0.05)	0.0099(0.0000)
19.59	124.0	0	0.22(0.02)	0.0099(0.0001)
	127.0	7×10^{-3}	0.20(0.08)	0.0103(0.0002)
	130.0	1×10^{-2}	0.12(0.03)	0.0109(0.0000)

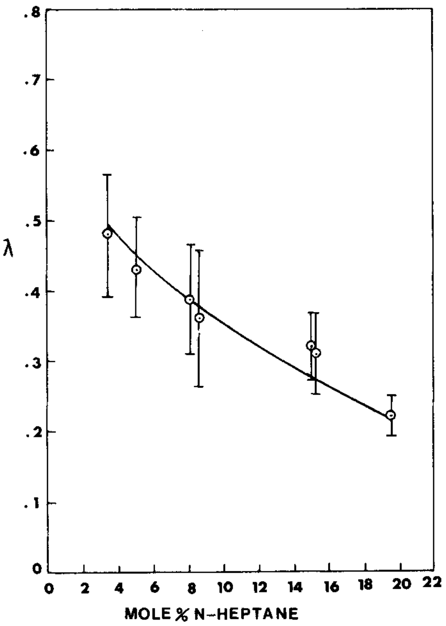

Fig. 5. λ vs. composition.

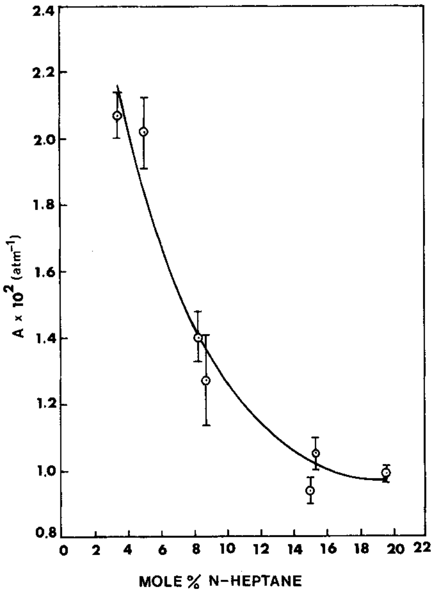

Fig. 6. A vs. composition.

tion of the data is completed by the specification of the locus of points of maximum compressibility $\hat{P}(T)$ together with the corresponding volumes $\hat{V}(T)$. This locus (Table 2) lies close to the coexistence surface and probably in the 1-phase region, but neither the present data nor those defining the coexistence surface (Kay, 1938; Mehra and Thodos, 1965) are sufficiently accurate to determine the latter point with certainty.

If Equation (1) applies at values of σ, no matter how small, $k_{T,x}$ may be said to diverge at the critical locus. Most empirical equations of state, including the Redlich-Kwong (RK) or Flory-Orwoll-Vrij (FOV) equations predict, on the other hand, that the compressibility of mixtures is finite everywhere. Regardless of whether or not the present data justify the claim that $k_{T,x}$ diverges at the critical locus (see below) the RK and FOV equations fail qualitatively to predict the behavior of that variable close to the critical locus. This can be seen, for example, by calculating $k_{T,x}$ according to the Redlich-Kwong (RK) equation, calibrated by the methods of Chueh and Prausnitz to reproduce the experimental critical locus (Chueh and Prausnitz, 1967).** If the compressibility is now calculated according to Equation (11) of Wu and Ehrlich (1973) at the critical locus, the finite value, designated by $k^c_{T,x}$, is obtained. The corresponding pressure is quite different from the pressure P^m at which the RK equation

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** The values of the equation of state parameters may be found in Tables 1 and 3 of Wu and Ehrlich (1973).

predicts a maximum value $k^m{}_{T,x}$ which, in general, greatly exceeds $k^c{}_{T,x}$. Figure 7 illustrates the convergence of the compressibility to the value $k^m{}_{T,x}$ predicted by the RK equation in contrast to the divergence of the experimental results.

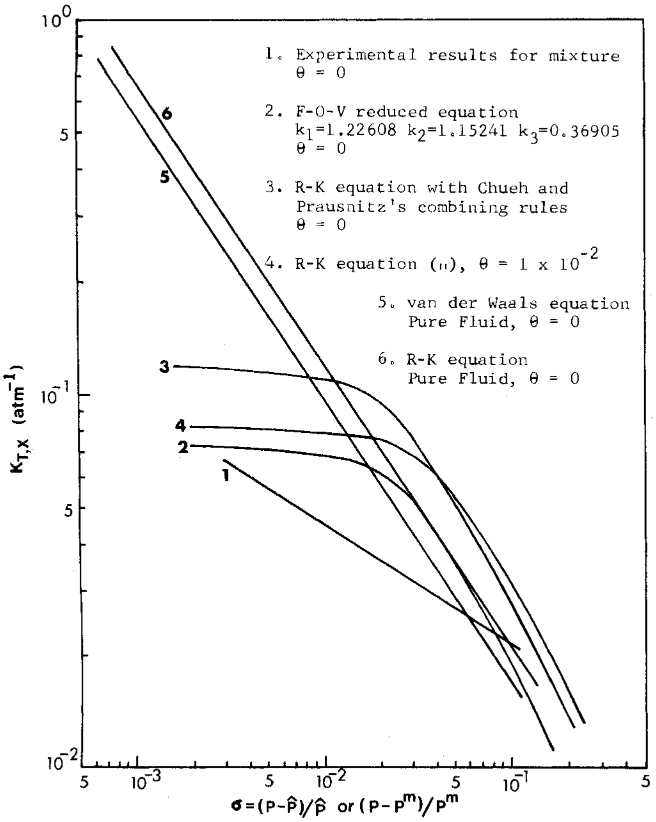

Fig 7. $k_{T,x}$ vs. σ found by experiment and calculated according to equations of state. X = 0.0347.

Figure 8, on the other hand, compares the experimental compressibility as a function of composition at a small but experimentally accessible distance from the critical locus with $k^c{}_{T,x}$. These arbitrary and erroneous compressibilities calculated according to empirical equations of state testify to their inconsistencies. It is clear that over a substantial portion of the supercritical region ($\sigma \leqq 0.1$) Equation (1) represents the isothermal compressibility far better than do the equations of state considered here which contain basic flaws in as much as they lead to a sharp convergence of $k_{T,x}$ in conflict with the experimental results, and to a severe underestimate of $k_{T,x}$ near the critical point.

The predictive value of Equation (1) can not yet be fully assessed. A knowledge of $A(x)$ and $\lambda(x)$ allows an estimate of $k_{T,x}$ along all critical and near-critical isotherms in the pressure range $10^{-3} < \sigma \leqq 10^{-1}$ for ethane-*n*-heptane at all compositions over which such data are available and serves to unify such data. It might be possible to extend the method to compositions not investigated and, eventually, to mixtures for which only the critical locus is known. As was shown, equations of state cannot predict the absolute value of the compressibility in the critical region nor the correct dependence on pressure. The dependence of $k^c{}_{T,x}$ or $k^m{}_{T,x}$ on composition shown in Figure 9 should, however, reflect qualitatively the true behavior of $k_{T,x}$ at a small distance from the critical locus before critical fluctuations have become dominant. It is possible that the relation between the experimentally-significant parameter λ and the fictitious parameter $k^c{}_{T,x}$, shown in Figure 10, also holds for the descending branch of the critical locus ($0.23 < x < 1.00$). λ could then be calculated from $k^c{}_{T,x}$ without further experimental information. The idea receives some support from the fact that

TABLE 2. CRITICAL CONSTANTS FOR MIXTURES AND EXPERIMENTALLY DETERMINED $\hat{P}$ AND $\hat{V}$

Mole % heptane	T_c, °C	P_c, atm	V_c, cc/mole	T, °C	$\hat{P}$, atm	$\hat{V}$, cc/mole
		Literature[a]			Experimentally determined[b],[c]	
3.47	50.8	59.52	131.0	50.8	59.699(±0.153)	139.5
	(50.8)	(59.52)		51.7	60.242(0.073)	141.7
				53.1	60.955(0.160)	143.5
5.04	59.0	63.94	133.5	54.3	61.410(0.105)	147.8
	(60.0)	(64.56)		60.0	64.497(0.106)	144.0
				62.0	65.893(0.150)	146.0
				65.0	66.725(0.305)	157.0
8.26	75.0	72.11	136.2	76.0	72.900(0.155)	144.0
	(78.0)	(72.79)		78.0	73.467(0.118)	148.0
				80.0	74.550(0.219)	149.0
8.69	77.0	72.79	146.8	80.0	74.583(0.153)	145.0
	(80.0)	(73.47)		81.5	74.722(0.179)	150.0
				84.0	76.095(0.139)	152.0
				86.4	77.021(0.180)	157.0
15.07	104	81.97	148.0	108.0	83.730(0.095)	151.0
	(109)	(83.33)		110.0	84.337(0.171)	155.0
				112.0	84.137(0.188)	161.5
15.26	105	82.99	148.5	108.0	83.763(0.108)	153.0
	(110)	(83.67)		110.0	84.469(0.283)	157.0
				112.0	83.880(0.319)	163.0
19.59	122	85.35	158.0	124.0	85.041(0.300)	159.0
	(130)	(86.71)		127.0	85.564(0.574)	164.0
				130.0	85.795(0.454)	170.0

[a] Critical temperatures and pressures are read from the smoothed curves of Kay (1938) and Mehra and Thodos (1965) which are listed in parentheses. The critical volumes are calculated and interpolated from Kay's data for the critical density and the average molecular weight.

[b] Values in the parentheses are in the 95% confidence range.

[c] The first set of values corresponding to each composition should correspond to the critical parameters T_c, P_c, V_c. T_c is chosen to correspond to the literature values; where these differ, an arbitrary choice is made. This makes the assignment of θ values somewhat uncertain. Note that θ has only a secondary effect on λ and A (Table 1).

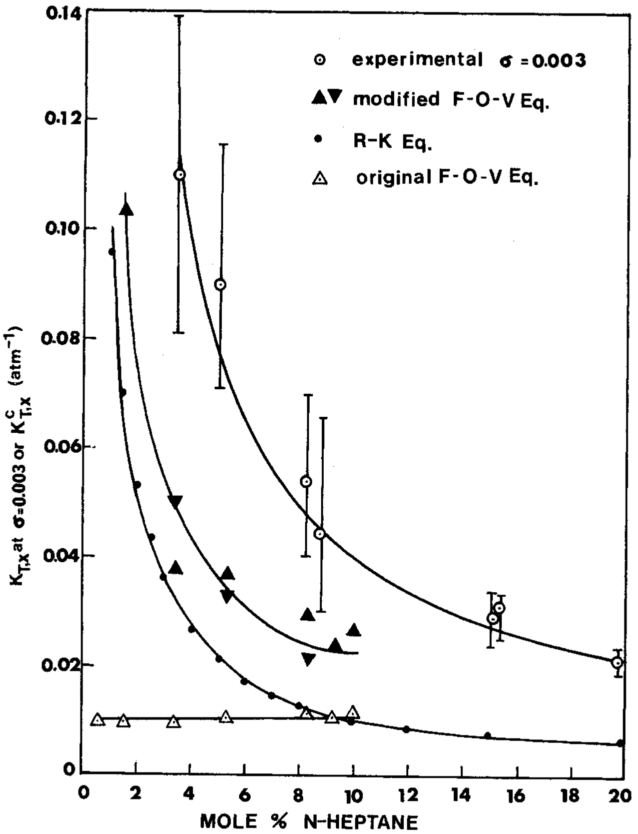

Fig. 8. $k_{T,x}$ at $\sigma = 0.003$ or $k^c_{T,x}$ vs. composition. $k_1 = 1.10195$, $k_2 = 1.11505$, $k_3 = 0.36473$ (▲); $k_1 = 1.22608$, $k_2 = 1.15241$, $k_3 = 0.36905$ (▲).

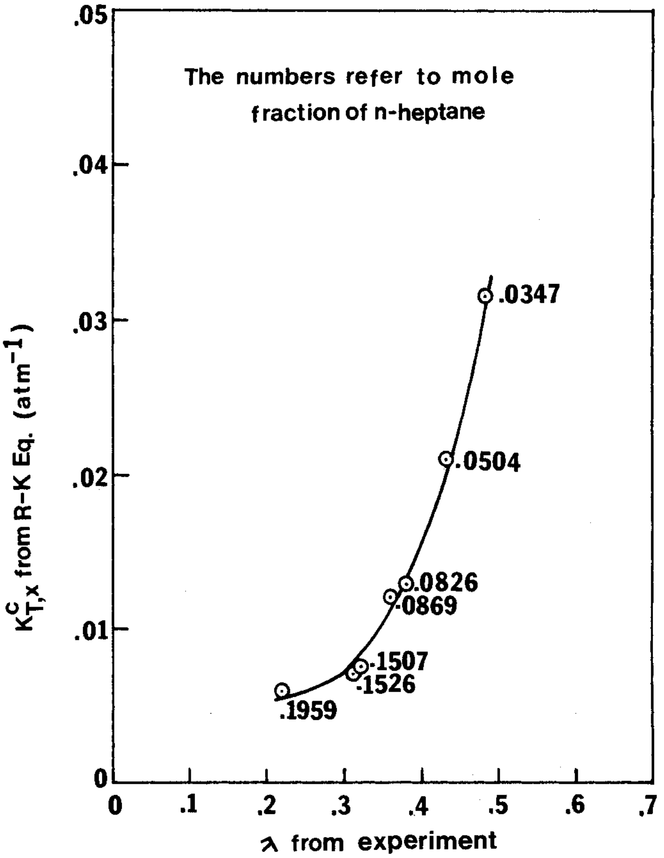

Fig. 10. $k^c_{T,x}$ vs. λ.

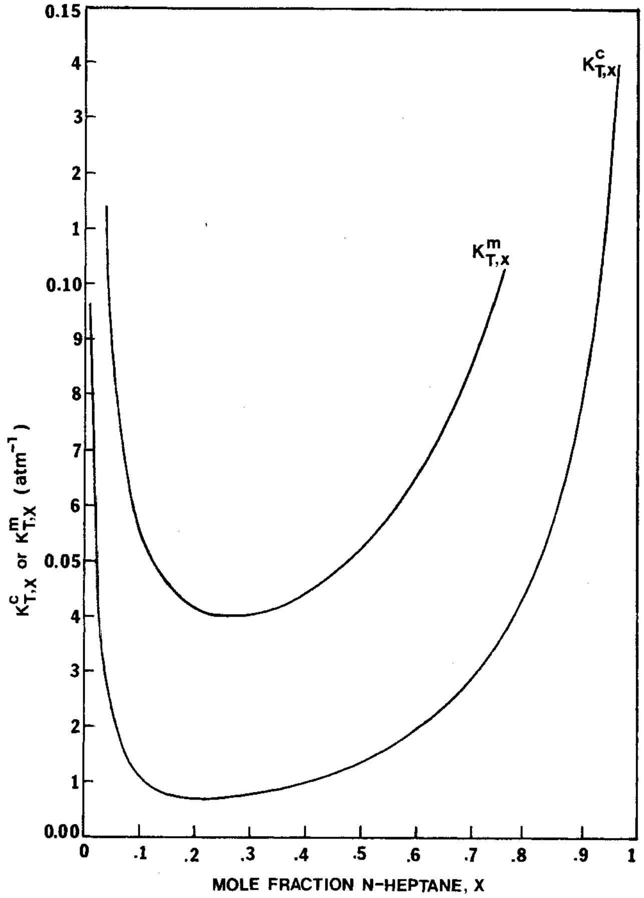

Fig. 9. $k^c_{T,x}$ and $k^m_{T,x}$ vs. composition.

the maximum pressure on the critical locus represents a maximum in density (Kay, 1938) together with a minimum in the fictitious compressibilities $k^c_{T,x}$ and $k^m_{T,x}$ (Figure 9) and the possibility that this may coincide with minima in λ and A (Figures 5 and 6). Further data are needed to test these methods and extend them to other mixtures.

RELATION TO THEORY OF CRITICAL PHENOMENA

Equation (1) may be written as

$$k_{T,x} = C\,(P - \hat{P})^{-\lambda} \tag{2}$$

where $\hat{P} = P_c$ at $\theta = 0$ and C is a constant. Equation (2) is identical in form to expressions describing the divergence of a number of thermodynamic parameters, including $k_{T,x}$, at the critical point, according to theories which do not assume the analyticity of the Helmholtz free energy at the critical point (Fisher, 1967; Rowlinson, 1969). The theory, which specifies and relates the magnitude of the exponents for different parameters, is generally well developed and tested for pure fluids, but less so for mixtures (Griffiths and Wheeler, 1970). It is important to note that the theory deals with the limiting values of the exponents at the critical point, and it is not to be inferred that the values of λ reported here necessarily represent such limiting components. On the basis of the data alone that possibility must, however, not be excluded, although the arguments of Griffiths and Wheeler (1970) do not appear to allow for a value of λ greater than 0.2. Since the theory is not sufficiently well developed to make numerical predictions of the amplitude C and the exponent λ for mixtures, and since equations of state fail near the critical point, the empirical methods based on Equations (1) and (2) appear to provide the best practical estimates of $k_{T,x}$ near the critical locus at this time.

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NOTATION

T = temperature
P = pressure
V = molar volume
$k_{T,x}$ = isothermal compressibility
σ = $(P - \hat{P})/\hat{P}$
θ = $(T - T_c)/T_c$
A, C = constants
λ = experimental exponent defining divergence of $k_{T,x}$ according to Equation (1) or (2)
σ_0 = an arbitrary reduced reference pressure (σ = 0.1)
$k^c{}_{T,x}$ = the (erroneous) value of $k_{T,x}$ predicted by an empirical equation of state upon substitution of the critical value for the independent variable
$k^m{}_{T,x}$ = the (erroneous) maximum value of $k_{T,x}$ calculated by an empirical equation of state when the pressure (and volume) are allowed to vary
P^m = pressure corresponding to $k^m{}_{T,x}$
k_1, k_2, k_3 = exponents in FOV equation
$\wedge$ = value of a given independent variable (P or V) at which $k_{T,x}$ shows a singularity
$_c$ = the critical value of a given independent variable

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Infinite Dilution Diffusion Coefficients in Liquids

The extension of the Enskog theory by Tham and Gubbins for the calculation of diffusivities is applied to the prediction of infinite dilution diffusion coefficients in binary organic systems. The resulting expression is a function only of the size and mass of the diffusing species. Excellent agreement is obtained for nonassociating *n*-alkane mixtures as well as for associated systems. Extension of the expression to alcohol and aqueous systems is shown to require only an empirical correction factor. It is also shown that the quantity $D_{ij}{}^\infty\ \eta_j\ M_j/\rho_j T$ is independent of temperature for all systems.

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SCOPE

The use of statistical mechanical approaches in the prediction of diffusion has provided much insight into the analysis of experimental data. Enskog and subsequent extensions to binary systems have analyzed the transport properties of dense fluids in terms of a rigid sphere model (Chapman and Cowling, 1952). Loflin and McLaughlin (1969), by an application of the Rice-Allnatt theory (1961), have described diffusion in a mixture of Lennard-Jones fluids. In these approaches the diffusion coefficient is described in terms of the size and mass of the diffusing species, as well as the interactions encountered by the species under study. However, these theories have been shown to provide only qualitative agreement with data and, as such, are of only limited value.

In this work the rigid sphere model of a dense fluid will be utilized as a basis for the development of a predictive equation for diffusion in binary systems at infinite dilution. The rigid sphere molecule exhibits infinite repulsion at collision and zero interaction at all other intermolecular distances. A description of diffusion in pure fluids exhibit-