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Determination of Binary Mixture Vapor–Liquid Critical Densities from Coexisting Density Data

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Two-phase vapor–liquid equilibrium (VLE) isochores for binary mixtures are defined as the thermodynamic paths along which the overall density and composition are fixed. Data along such isochores are generated from a modified Leung–Griffiths model fit to experimental data for the binary system nitrogen–methane. The behavior of the liquid volume fraction along these isochores is found to be similar to that for pure fluids. Rectilinear diameters for varying overall densities (fixed composition) are seen to be nearly coincident. Straight-line diameters and the critical liquid volume fraction method are utilized to predict critical densities using data near and removed from the critical point. Both methods give acceptable results but the critical liquid volume fraction method is more accurate. A critical literature review of the need for binary mixture critical densities is presented and a proposed experimental procedure is given for the determination of mixture critical densities.

KEY WORDS: coexistence densities; critical density; liquid volume fraction; mixtures; nitrogen–methane; phase equilibria; rectilinear diameter; two-phase isochores.

1. INTRODUCTION

Critical density loci of binary mixtures for vapor–liquid equilibrium (VLE) are in general known with much less certainty than loci of critical temperatures or pressures. Gravity and other factors cause extreme difficulties in the direct experimental measurement of critical densities even of pure fluids [1, 2] and these problems are significantly more severe for binary mixtures [3, 4].

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As a result, pure fluid critical densities have often been inferred from coexisting densities near the critical as an alternative to direct measurement. One approach frequently used is to extrapolate a rectilinear diameter, usually assumed to be a straight line on a temperature–density plot, to a "known" critical temperature [5]. This approach has been attempted on occasion for mixtures along loci of fixed composition [6, 7], although its applicability there is much more questionable.

Van Poolen and co-workers [8–11] have developed an alternate method based on the observation that the liquid volume fraction approaches one-half at the critical point along the two-phase critical isochore. Their method can be used to check the self-consistency of saturated density correlations [8], to predict accurately the critical density from saturation densities either close to or somewhat removed from the critical point [9, 11], and to predict saturation densities of one phase, liquid or vapor, given those of the other phase [9, 10]. An objective of this paper is to apply Van Poolen's approach, for the first time, to binary mixtures and to compare it to the use of a straight-line rectilinear diameter.

A two-phase isochore can be defined for a binary mixture, but its properties are somewhat different for a mixture than for a pure fluid. Also, it is not the thermodynamic path along which vapor–liquid equilibrium density data have been taken in most previous experiments. Therefore, our initial application of the liquid volume fraction method is necessarily in reference to a correlation of a coexistence surface based on experimental data, not directly to experimental results.

Traditional equations of state for binary mixtures qualitativaly predict a correct VLE surface but typically the phase equilibrium calculations fail to converge or are inaccurate within the critical region. However, recently Rainwater, Moldover, and co-workers [12–17] have extended the model of Leung and Griffiths [18] to obtain accurate VLE correlations for more than 20 binary mixtures in the critical region. Unlike classical equations of state, their model incorporates scaling-law critical exponents and thus approaches the correct critical asymptotic limit. In its present form it does not contain the higher-order nonanalytic terms of revised and extended scaling [19].

In this paper, the liquid volume fraction technique is generalized to binary mixtures and applied to the results of a correlation of Rainwater and Moldover in lieu of direct experimental data. It is instructive to choose a specific prototype mixture, which we take to be nitrogen + methane. Our discussion is based on the correlation [14] of the VLE data of Bloomer and Parent [20].

Nitrogen + methane is a convenient mixture for several reasons. The relative volatility is sufficiently large that mixture behavior, e.g., retrograde condensation, is clearly in evidence, yet not so large that the assumptions of the model break down. It is of industrial importance as a model for certain samples of natural gas. In addition to the work of Bloomer and Parent [20], VLE data for this mixture (without saturation density information) have been measured independently by Cines et al. [21], Kidnay et al. [22], and Stryjek et al. [23]. The fit to the constant-composition data of Bloomer and Parent yields a good agreement with these three aforementioned isothermal experiments and, particularly, is in good agreement with Stryjek et al. The discrepancies between the correlation and the latter measurements appear to be significantly smaller than the discrepancies among the three experiments.

A question arises as to whether our conclusions apply to actual experimental data or merely to a theoretical model. In a strict sense, we are demonstrating some properties of a mathematical correlation, and certain detailed behavior, e.g., the absence of the last term in Eq. (20) below, is almost certainly an artifact of the model. However, since the model is a faithful representation of the data of Bloomer and Parent, and others, we have confidence that our conclusions, for the most part, are applicable to real binary mixtures.

In Section 2, the modified Leung–Griffiths model is very briefly summarized, and in Section 3 the binary mixture two-phase isochore is defined and its determination from the model is explained. The behavior of the liquid volume fraction is also noted. The nature of a rectilinear diameter for binary mixtures is described in Section 4. Various fitting functions previously used for pure fluid coexisting densities are applied in Section 5 to the mixture critical isochore. In Section 6 we note the large number of binary mixtures for which critical temperatures are known but critical densities are not, and in the following two sections an experimental and correlating method is developed to establish critical density loci for such mixtures. Results are summarized in Section 9.

2. THE MODIFIED LEUNG–GRIFFITHS MODEL

The system under consideration is a normal (i.e., nonazeotropic) binary mixture with a continuous critical line and coexistence surface. In pressure (P)–temperature (T) space the coexistence region is bounded from above by the critical locus and from the sides by the vapor pressure curves of the two pure fluids. Within this region, at any (P, T) point vapor of density ρ^{v} and composition x^{v} coexists with liquid of density ρ^{l} and composition x^{l}. In the absence of azeotropy, and away from the critical locus, $x^{\mathrm{v}} \neq x^{l}$.

The Leung–Griffiths model is expressed in terms of “field variables,” defined by Griffiths and Wheeler [24] as those variables which are equal for both liquid and vapor. The fundamental field variables are P, T, and the chemical potentials μ_1 and μ_2; functions of these variables are also field variables. In contrast, "density variables" such as ρ and x differ between liquid and vapor.

The independent field variables of the Leung–Griffiths model as modified by Rainwater and Moldover [14, 16] are ζ and t, where

$$\zeta = \frac{e^{\mu_1/RT}}{Ke^{\mu_2/RT} + e^{\mu_1/RT}} \tag{1}$$

where R is the gas constant, and

$$t = \frac{T - T_c(\zeta)}{T_c(\zeta)} \tag{2}$$

Also, on the critical line

$$x = 1 - \zeta \tag{3}$$

In earlier work [12–15, 17], K in Eq. (1) was assumed to be constant. Recently it has been shown [16] that K can be a temperature-dependent function without changing the thermodynamic expressions for density and composition, although other variables such as the enthalpy are changed.

Our convention is that fluid 1 is the less volatile component, here methane, and $x = 1$ is pure fluid 2. Since $\mu_1 \to -\infty$ for pure fluid 2, and vice versa, $\zeta = 0$ if $x = 1$ and conversely. If $T_c(x)$ is a monotonically decreasing function of x, a temperature-dependent K exists such that Eq. (3) holds exactly along the critical locus.

It is assumed within the model that, on the coexistence surface, lines of constant ζ are given by

$$\frac{P}{T} = \frac{P_c(\zeta)}{T_c(\zeta)} [1 + C_3(\zeta)(-t)^{1.9} + C_4(\zeta)\,t + C_5(\zeta)\,t^2 + C_6(\zeta)\,t^3] \tag{4}$$

For $\zeta = 1$ or 0, Eq. (4) represents a fit to the vapor pressure curve of fluid 1 or 2, respectively, and those fit coefficients are denoted by $C_i^{(1)}$ and $C_i^{(2)}$. It is further assumed that the ζ-dependent coefficients may be found by linear interpolation, i.e.,

$$C_i(\zeta) = C_i^{(2)} + \zeta[C_i^{(1)} - C_i^{(2)}]; \qquad i = 3, 4, 5, 6 \tag{5}$$

Equations (4) and (5) imply that loci of constant ζ form a nearly parallel set of curves; see Fig. 1 in Ref. 14. Unlike Eq. (3), there is not enough freedom in the definition of ζ to make Eqs. (4) and (5) hold in general. However, it is found empirically that these are excellent approximations as long as the molecules of fluids 1 and 2 are not too dissimilar.

A further assumption of the model is that

$$\rho = \rho_c(\zeta)[1 \pm C_1(\zeta)(-t)^\beta + C_2(\zeta)\,t] \tag{6}$$

where plus refers to liquid and minus to vapor, and $\beta = 0.355$. Thus, along loci of constant ζ, coexisting densities behave like those of a pure fluid with a straight rectilinear diameter. This is not to be confused with loci of constant x (dew-bubble curves), which in general have a shape quite different from that of Eq. (6). The ζ dependence of C_1 and C_2 in general is somewhat more complicated than indicated by Eq. (5) [14, 16].

In the two-phase region, for each (P, T) or (ζ, t) point, a liquid of composition x^l coexists with a vapor of composition x^v. Within the model, x^l and x^v are given as functions of ζ and t as well as derivatives of the critical line and some adjustable parameters. The expressions are somewhat lengthy [14–17] and are not repeated here.

To calculate dew-bubble curves, first a set of t values in essentially a geometric series is constructed to achieve more resolution near the critical point. Then, for each t, the equations for $x^l(\zeta, t)$ and $x^v(\zeta, t)$ are inverted numerically to find the values of ζ such that x^l and/or x^v equal the specified composition. With ζ and t determined, the pressure, temperature, and density of the dew or bubble point are given by Eqs. (2), (4), and (6).

3. TWO-PHASE ISOCHORES

A point (P, T) on the coexistence surface corresponds to a particular liquid state in equilibrium with a particular vapor state. However, we can add a new dimension to the description by varying the relative amounts of liquid and vapor or changing the height of the meniscus. A single (P, T) point thus corresponds to a range of two-phase states which can be characterized by an overall composition x_T and an overall density ρ_T, where by our convention

$$x^l(P, T) \leqslant x_T \leqslant x^v(P, T) \tag{7}$$

and

$$\rho^l(P, T) \geqslant \rho_T \geqslant \rho^v(P, T) \tag{8}$$

The totality of two-phase states of a given x_T or a given ρ_T covers a bounded two-dimensional region in P–T space. For example, the former is the "inside" of the dew-bubble curve for composition x_T.

However, if *both* x_T and ρ_T are specified, there is only one degree of freedom (discussed in more detail later) and the set of such two-phase states falls onto a one-dimensional curve in P–T space. We define a "two-phase isochore" to be such a locus of fixed x_T and ρ_T. A critical two-phase isochore is one for which $\rho_T = \rho_c(x_T)$ and terminates at the critical point for composition x_T. If $\rho_T \neq \rho_c(x_T)$, the isochore terminates on the dew-bubble curve for composition x_T and short of the critical locus, as shown in Fig. 1. Two-phase isochores can be defined for a pure fluid as well. The main differences are that, for a mixture, the liquid and vapor have different compositions and that, for a pure fluid, all two-phase isochores follow the same curve in P–T space, whereas two-phase isochores of different ρ_T fall on different P–T curves for a mixture.

Unlike a pure fluid, it is important for mixture analysis to distinguish between mass and molar density. In our model, ρ is the molar density and x is the mole fraction of fluid 2. Let N be the total number of moles of a

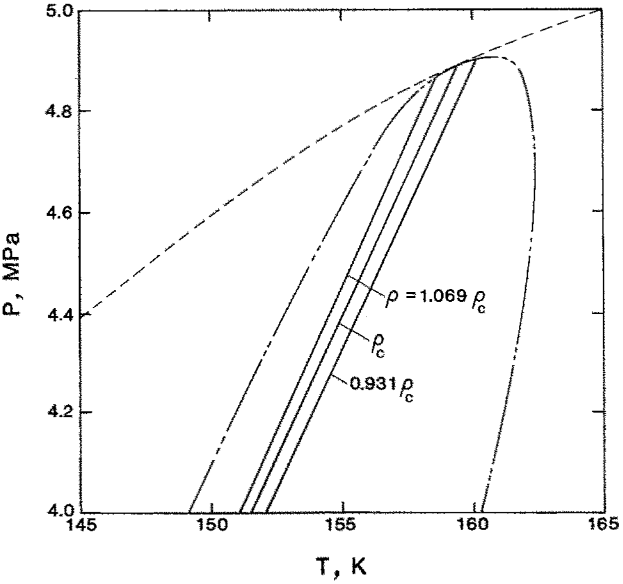

Fig. 1. Two-phase isochores near the critical point of a nitrogen + methane mixture with $x_T(N_2) = 0.5088$. The dashed line is the critical line, the broken line is the dew-bubble curve, and the solid lines are isochores with densities as indicated. Note that only the critical isochore in the center extends to the critical line. The same qualitative pattern applies for all compositions.

mixture, V_{l} the liquid volume, and V_{v} the vapor volume. Amount-of-substance balance overall and for fluid 2 yields, respectively,

$$N=\rho^{l}V_{l}+\rho^{\mathrm{v}}V_{\mathrm{v}} \tag{9}$$

$$Nx_{\mathrm{T}}=x^{l}\rho^{l}V_{l}+x^{\mathrm{v}}\rho^{\mathrm{v}}V_{\mathrm{v}} \tag{10}$$

Solving for the volumes yields

$$V_{l}=\frac{N(x^{\mathrm{v}}-x_{\mathrm{T}})}{\rho^{l}(x^{\mathrm{v}}-x^{l})} \tag{11}$$

and

$$V_{\mathrm{v}}=\frac{N(x_{\mathrm{T}}-x^{l})}{\rho^{\mathrm{v}}(x^{\mathrm{v}}-x^{l})} \tag{12}$$

The total density of the mixture is

$$\rho_{\mathrm{T}}=\frac{N}{V_{l}+V_{\mathrm{v}}}=(x^{\mathrm{v}}-x^{l})\left[\frac{x^{\mathrm{v}}-x_{\mathrm{T}}}{\rho^{l}}+\frac{x_{\mathrm{T}}-x^{l}}{\rho^{\mathrm{v}}}\right]^{-1} \tag{13}$$

and thus is expressed in terms of quantities that can be calculated from the algorithm described in the preceding section for a given x_{T}.

The liquid volume fraction X_{LV} is defined as

$$X_{\mathrm{LV}}=\frac{V_{l}}{V_{\mathrm{T}}} \tag{14}$$

where $V_{\mathrm{T}}=V_{l}+V_{\mathrm{v}}$. From a rearrangement of Eq. (9),

$$\rho_{\mathrm{T}}V_{\mathrm{T}}=\rho^{l}V_{l}+\rho^{\mathrm{v}}(V_{\mathrm{T}}-V_{l}), \tag{15}$$

Eqs. (14) and (15) then give

$$X_{\mathrm{LV}}=\frac{\rho_{\mathrm{T}}-\rho^{\mathrm{v}}}{\rho^{l}-\rho^{\mathrm{v}}} \tag{16}$$

and a similar calculation based on Eq. (10) leads to

$$X_{\mathrm{LV}}=\frac{\rho_{\mathrm{T}}x_{\mathrm{T}}-\rho^{\mathrm{v}}x^{\mathrm{v}}}{\rho^{l}x^{l}-\rho^{\mathrm{v}}x^{\mathrm{v}}}. \tag{17}$$

Alternately, Eq. (13) can be derived by equating the right sides of Eqs. (16) and (17) and solving for ρ_{T}. Equating Eqs. (16) and (17) yields a relationship between the intensive variables in addition to those relationships between temperature, pressure, chemical potentials, and molar fractions used to obtain Gibbs' phase rule. Thus if ρ_T and x_T are held constant, a system with one degree of freedom obtains (as stated previously) and a two-phase isochore falls on a single curve in a fashion similar to pure fluids; see Fig. 1.

The numerical codes to calculate dew-bubble curves according to the modified Leung–Griffiths model have been extended to calculate two-phase isochores. As described in the previous section, for a given t, values of ζ, denoted here by ζ_l and ζ_v, are determined, where $x^l(\zeta_l, t) = x_T$ and $x^v(\zeta_v, t) = x_T$, and $\zeta_l < \zeta_v$. Then the value of ζ within the interval $\zeta_1 < \zeta < \zeta_v$ is found numerically such that, for the given t and ρ_T, Eq. (13) is satisfied. From this ζ and t, the pressure, temperature, and liquid and vapor compositions and densities can be calculated for such a point on the two-phase isochore. An input array of t values yields an output array of points along the isochoric locus.

Some sample output is given in Tables I–III based on the fit by Rainwater and Moldover [14] to the nitrogen + methane data of Bloomer and Parent [20], where $x_T(N_2) = 0.5088$ is one of the experimentally measured isopleths. Table II describes the critical isochore, $\rho_T = \rho_c$, while Table I describes an isochore somewhat below critical ($\rho_T/\rho_c = 0.931$) and Table III describes one somewhat above critical ($\rho_T/\rho_c = 1.069$). Note that $T_c = 159.48$ K, $P_c = 4.8967$ MPa, and $\rho_c = 11.433$ kmol · m^{-3}.

Table I. Two-Phase Isochore for $x_T(N_2) = 0.5088$ and $\rho_T/\rho_c = 0.931$

Pressure (MPa)	Temperature (K)	ρ^l (kmol · m^{-3})	ρ^v (kmol · m^{-3})	x^l	x^v	X_{LV}
4.9138	160.311	12.2069	10.6403	0.4844	0.5089	0.00231
4.9070	160.241	12.5826	10.2687	0.4795	0.5158	0.16229
4.8838	160.017	13.2067	9.6584	0.4721	0.5281	0.27787
4.8190	159.421	14.0729	8.8304	0.4634	0.5470	0.34597
4.6017	157.483	15.5396	7.4936	0.4528	0.5836	0.39152
4.3085	154.866	16.7586	6.4551	0.4476	0.6176	0.40657
4.0321	152.348	17.6516	5.7391	0.4459	0.6443	0.41176
3.7704	149.901	18.3867	5.1784	0.4456	0.6671	0.41381
3.5225	147.514	19.0251	4.7124	0.4463	0.6874	0.41444
3.2875	145.180	19.5968	4.3110	0.4476	0.7057	0.41432
3.0649	142.895	20.1193	3.9571	0.4492	0.7226	0.41375
2.8542	140.655	20.6036	3.6398	0.4511	0.7384	0.41290
2.6548	138.458	21.0571	3.3519	0.4533	0.7531	0.41187

Table II. Two-Phase Isochore for $x_T(N_2) = 0.5088$ and $\rho_T/\rho_c = 1.00$

Pressure (MPa)	Temperature (K)	ρ^l (kmol · m^{-3})	ρ^v (kmol · m^{-3})	x^l	x^v	X_{LV}
4.8932	159.441	12.2182	10.6500	0.4974	0.5219	0.49934
4.8864	159.374	12.5942	10.2780	0.4925	0.5287	0.49870
4.8632	159.155	13.2188	9.6669	0.4850	0.5409	0.49728
4.7986	158.573	14.0855	8.8378	0.4762	0.5596	0.49455
4.5819	156.677	15.5524	7.4986	0.4651	0.5954	0.48847
4.2898	154.114	16.7711	6.4580	0.4593	0.6285	0.48240
4.0146	151.649	17.6636	5.7405	0.4570	0.6544	0.47744
3.7542	149.252	18.3980	5.1786	0.4563	0.6763	0.47313
3.5076	146.914	19.0357	4.7115	0.4564	0.6958	0.46924
3.2740	144.626	19.6067	4.3093	0.4572	0.7135	0.46568
3.0527	142.385	20.1285	3.9547	0.4583	0.7297	0.46237
2.8432	140.187	20.6121	3.6370	0.4598	0.7449	0.45926
2.6450	138.029	21.0649	3.3487	0.4614	0.7591	0.45632

It is seen that the liquid volume fraction behaves very much like that of a pure fluid [8–11]. On the critical isochore X_{LV} approaches one-half, whereas on the isochore below critical it reaches a maximum value and falls abruptly toward the limit of zero, and on the isochore above critical it rises abruptly toward a limiting value of one.

Table III. Two-Phase Isochore for $x_T(N_2) = 0.5088$ and $\rho_T/\rho_c = 1.069$

Pressure (MPa)	Temperature (K)	ρ^l (kmol · m^{-3})	ρ^v (kmol · m^{-3})	x^l	x^v	X_{LV}
4.8742	158.685	12.2274	10.6579	0.5087	0.5331	0.99623
4.8674	158.619	12.6038	10.2855	0.5038	0.5399	0.83529
4.8443	158.406	13.2288	9.6737	0.4963	0.5521	0.71681
4.7799	157.836	14.0959	8.8436	0.4873	0.5705	0.64340
4.5639	155.979	15.5631	7.5025	0.4758	0.6056	0.58546
4.2730	153.467	16.7815	6.4601	0.4695	0.6379	0.55824
3.9990	151.048	17.6735	5.7412	0.4667	0.6629	0.54312
3.7399	148.696	18.4074	5.1783	0.4655	0.6842	0.53243
3.4946	146.400	19.0445	4.7104	0.4652	0.7030	0.52403
3.2622	144.153	19.6150	4.3076	0.4655	0.7201	0.51703
3.0421	141.950	20.1362	3.9525	0.4662	0.7357	0.51097
2.8337	139.788	20.6192	3.6343	0.4672	0.7504	0.50560
2.6365	137.664	21.0714	3.3457	0.4684	0.7641	0.50075

4. NEAR-COINCIDENCE OF RECTILINEAR DIAMETERS OF TWO-PHASE ISOCHORES

In this section we describe an observation which can be exploited to obtain simple and accurate measurements of binary mixture critical densities. As shown in Tables I–III, for each point on the two-phase isochore there are a pair of coexisting densities, and along such an isochore these densities are functions of T. We thus define $\rho_i^l(\rho_T, x_T, T)$ and $\rho_i^v(\rho_T, x_T, T)$ and proceed to define a rectilinear diameter *for the isochore* (i), $\rho_R(\rho_T, x_T, T)$ by

$$\rho_R(\rho_T, x_T, T) = \tfrac{1}{2}\{\rho_i^l(\rho_T, x_T, T) + \rho_i^v(\rho_T, x_T, T)\} \qquad (18)$$

For $\rho_T > \rho_c(x_T)$, these functions terminate at a temperature below $T_c(x_T)$, whereas for $\rho_T < \rho_c(x_T)$ in the retrograde region they terminate above $T_c(x_T)$. The densities ρ_i^l and ρ_i^v are not to be confused with the liquid and vapor densities on the dew-bubble curve for a composition x_T. Indeed, the latter densities correspond to liquid and vapor states which do not coexist; for example, they are at different pressures for the same temperature.

Sample results from the nitrogen + methane correlation are plotted in Fig. 2 for $x_T(N_2) = 0.5088$ and the two-phase isochores for $\rho_T = 0.931\rho_c$, $\rho_T = \rho_c$, and $\rho_T = 1.069\rho_c$. Also shown is the dew-bubble curve for $x_T(N_2) = 0.5088$ and its region of retrograde condensation above $T_c(x_T) = 159.48$ K. From this and similar diagrams, two observations can be made. First, the rectilinear diameters are nearly straight lines. Second, the various different rectilinear diameters nearly coincide, i.e., they nearly fall on the *same* straight line. Mathematically, this implies that $\rho_R(\rho_T, x_T, T)$ is almost independent of ρ_T, at least for ρ_T within about 7% of ρ_c.

From Eq. (6), the modified Leung–Griffiths model has the built-in constraint that the rectilinear diameter for a line of constant ζ is a straight line. Therefore, if the two-phase isochores were nearly identical to loci of constant ζ, the first observation would be a trivial artifact of the model. In fact, although two-phase isochores are qualitatively similar to curves of fixed ζ, along an isochore ζ shows considerable variation. For example, along the critical isochore $\zeta = 0.4912$ at $t = 0$, as required by Eq. (3), but $\zeta = 0.381$ at $t = -0.9$. Therefore, the nearly straight rectilinear diameters are probably a property of the actual data rather than an artifact of the model.

In Fig. 3 an expanded view of the isochore rectilinear diameters is shown. It is seen that they do not *exactly* coincide, and we can see no mathematical reason to expect that they should. However, the differences

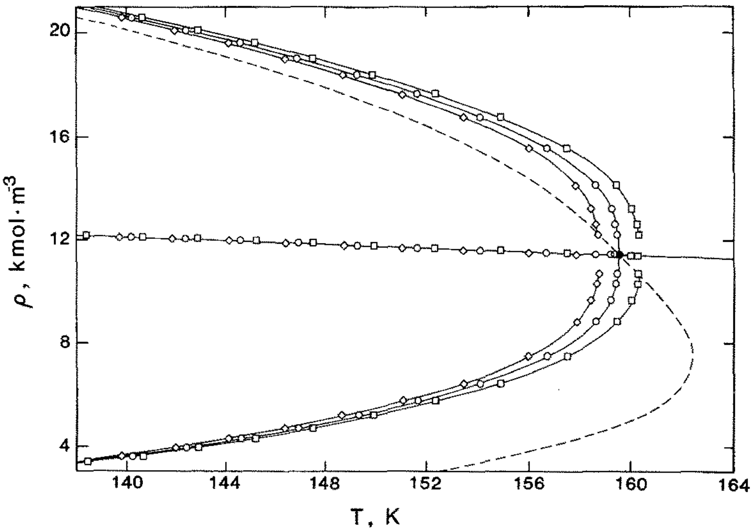

Fig. 2. Coexisting densities along two-phase isochores for the nitrogen + methane mixture where $x_T(N_2) = 0.5088$: (○) $\rho = \rho_c$; (◇) $\rho = 1.069\rho_c$; (□) $\rho = 0.931\rho_c$; (●) critical point. The upper points are liquid densities, the lower points are vapor densities, and the middle points display the nearly straight, nearly coincident rectilinear diameters. Also shown is the dew-bubble curve (dashed line). Note that the isochores off critical do not close at the right since they terminate at a two-phase point.

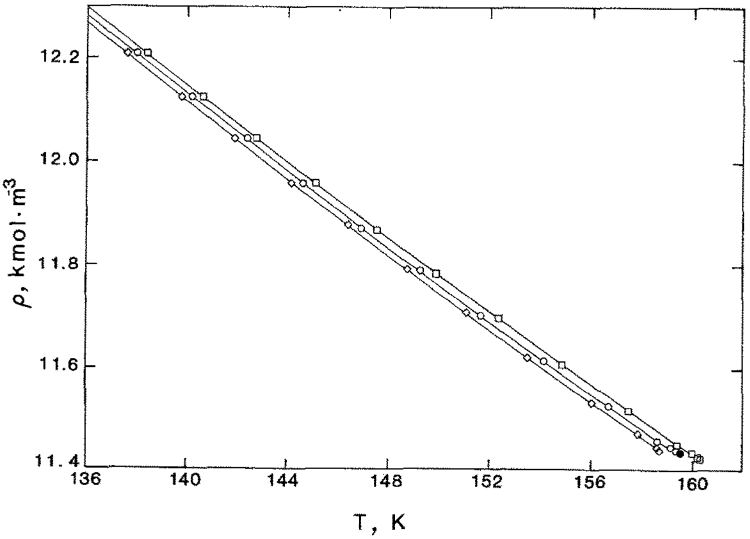

Fig. 3. Expanded view of the rectilinear diameters from Fig. 2. Note the greatly increased resolution of the density scale.

between them are exceptionally small. The pattern for other experimentally measured isopleths of the mixture nitrogen + methane is similar, except that for nitrogen-rich mixtures there is a noticeable, but essentially negligible, curvature of the rectilinear diameters.

For a verification of the above hypothesis, direct experimental data for two-phase isochores would be useful. It is a fairly common procedure in VLE experiments [25] to determine a dew or bubble point by observing the change in slope in P–T space of an isochore as it crosses the coexistence surface. However, usually the coexisting densities and compositions in the two-phase region are not monitored. We are aware of only one experiment in which they have been monitored, that of Schneider and Maass [26] on an equimolar mixture of ethylene and propylene. Since Schneider and Maass measured only the critical two-phase isochore, our hypothesis of the near-coincidence of rectilinear diameters for *different* isochores cannot be tested. The Schneider–Maass results are discussed further in the following section.

5. FIT OF THE CRITICAL TWO-PHASE ISOCHORE

For pure fluids, Van Poolen et al. [11] have considered the following three expressions to fit the rectilinear diameter and determine the critical density, where $\varepsilon = T_c - T$,

$$\rho^l + \rho^v = A + B\varepsilon, \tag{19}$$

$$\rho^l + \rho^v = A + B\varepsilon + C\varepsilon^{(1-D)}, \tag{20}$$

and

$$\rho^l + \rho^v = A + B\varepsilon^C(\rho_l - \rho_v) + D\varepsilon^E(\rho_l - \rho_v) \tag{21}$$

The methods are described in detail in Ref. 27. Measurements of ρ^l and ρ^v are assumed to be available for a set of $T < T_c$. It is further assumed that T_c (but not necessarily ρ_c) is known with precision, and thus ε is known for each data pair. Equations (19)–(21) are fit with A through E as adjustable parameters [or, in some cases, D in Eq. (20) or C and E in Eq. (21) held constant] by standard methods. The estimated critical density from these optimizations then is $\rho_c = A/2$.

Equation (19) describes a straight rectilinear diameter and is consistent with Eq. (6) for $\zeta = 0$ or 1, i.e., for the pure fluids. Equation (20) describes a rectilinear diameter with a "hook." Within revised and extended scaling [18] $D = \alpha \approx 0.1$, where α is the critical exponent characterizing the divergence of the specific heat at constant volume. Finally, Eq. (21) is a rearrangement of the truncated expansion

$$X_{\mathrm{LVC}} = \frac{\rho_c - \rho^v}{\rho^l - \rho^v} = \frac{1}{2}\left[1 - B\varepsilon^C - D\varepsilon^E\right] \tag{22}$$

where X_{LVC} is the critical liquid volume fraction; cf. Eq. (16).

Within simple scaling, which is all that is contained in the present form of the modified Leung–Griffiths model, the leading-order exponent in Eq. (22) is $C = 1 - \beta$, whereas within revised and extended scaling $C = 1 - \beta - \alpha$. Empirically it has been found [11] for pure ethylene and oxygen that $C \approx 0.5$ and $E \approx 1.0$ provide the optimal fit.

From the earlier discussion, we expect that Eqs. (19) and (21) are applicable to the critical two-phase isochore of a binary mixture within the model, whereas Eq. (20) is not appropriate since the model in its present form does not contain a rectilinear diameter hook. Efforts have commenced to incorporate revised and extended scaling into the Leung–Griffiths model so that a hook is present, but the results are very preliminary at the present time. In fitting the isochore to Eq. (21) we use the fixed values $C = 0.65 \approx 1 - \beta$ and $E = 1$.

As an example, we use as input the results in Table II for $x_T(N_2) = 0.5088$ and $\rho_T = \rho_c(x_T)$, first, over the entire range available and, second, over a range somewhat removed from critical, $138.029\ \mathrm{K} < T < 144.626\ \mathrm{K}$. These values are fit to Eqs. (19) and (21) in turn, and the "predicted" $\rho_c = A/2$ is compared with the known model $\rho_c = 11.433\ \mathrm{kmol \cdot m^{-3}}$.

Results are expressed as percentage error, i.e., $100 \times (A/2 - \rho_c)/\rho_c$. From the straight rectilinear diameter, Eq. (19), the error is -0.050% for the full interval and -0.292% for the interval away from critical, whereas from the liquid volume fraction, Eq. (21), the errors are -0.00183% for the full interval and -0.146% for the interval away from critical.

As can be seen, the fits to the critical isochore result in good estimates for the critical density whether one uses a straight line or the liquid volume fraction method. The results were good whether or not data were fit in the critical region. The fit of the complete data to the diameter from the critical liquid volume fraction, Eq. (21), was by far the best as can be seen by the small error in ρ_c estimated, i.e., -0.00183%.

We have also attempted fits of the experimental data of Schneider and Maass [26] for the equimolar two-phase isochore of ethylene + propylene to Eqs. (19) and (21). Some evidently anomalous data points were omitted from the fitting. Their data agree with the optimal fits of these equations to within 1.1%, but the scatter is considerably greater than what has been observed for high-quality pure fluid coexisting density data. From their description of the experimental method, the total fluid volume was approximately constant but may not have been kept constant to high precision.

Qualitatively, their results agree with our conclusions concerning the variation of coexisting compositions with temperature. Furthermore, they report that isochores for $\rho < \rho_c$ terminate in a vapor state at $T > T_c$ and those for $\rho > \rho_c$ terminate in a liquid state at $T < T_c$, again consistent with our previous discussion.

Further analysis would require construction of a modified Leung–Griffiths model for ethylene + propylene. To our knowledge, the only other VLE measurements on this mixture are those of Haselden et al. [7]. Although the critical line was thoroughly measured in Ref. 7, unfortunately very few dew- and bubble-point measurements were reported in the critical region, and thus the development of a modified Leung–Griffiths correlation would be highly problematical. We note in passing that, as is evident from Fig. 2, an extrapolation of the rectilinear diameter of the dew-bubble curve (rather than that of a two-phase isochore) would in general lead to substantially inferior estimates of the critical density.

6. CURRENT NEEDS FOR BINARY MIXTURE CRITICAL DENSITIES

In the remainder of this paper we consider the situation in which $T_c(x)$ is known with reasonable precision but $\rho_c(x)$ is unknown. We then recommend a method to determine $\rho_c(x)$ from a minimal amount of experimental measurement.

It is emphasized that, for binary mixtures, the lack of ρ_c data is by no means a hypothetical situation. For most pure fluids of interest some experimental measurements of the critical density, although sometimes of questionable precision, are available. However, there are many binary mixtures for which the critical temperature locus has been measured but the critical density locus has not.

Even for a mixture as important and basic as ethane + propane, there are to our knowledge no measurements of mixture critical densities or coexisting densities near critical. However, Maschke and Thodos [28] and Miksovsky and Wichterle [29] have collectively measured VLE loci in (P, x) along 17 different isotherms, so there is excellent information about the critical locus in pressure and temperature.

Empirically it is found that $T_c(x)$ is usually a very smooth function of x, so measurement of the critical temperature at four suitably spaced compositions in most cases suffices for an accurate representation of the critical temperature locus. Mixtures for which there are critical-region VLE measurements along at least four isotherms but no critical or critical-region coexisting density data include argon + krypton [30], krypton + methane [31], krypton + xenon [32], xenon + ethane [33], xenon + ethylene [34], carbon dioxide + dimethyl ether [35], carbon monoxide + methane [36], nitrous oxide + oxygen [37], and water + ethanol [38].

In addition, there have been critical region VLE measurements of other mixtures along at least four isopleths without accompanying density data. Such mixtures include propane + *n*-heptane [39], acetylene + propane and acetylene + propylene [40], dimethyl ether + propylene and dimethyl ether + carbon dioxide [41], benzene + hexafluorobenzene [42], hydrogen chloride + propane [43, 44], and hydrogen chloride + krypton [43, 45].

Furthermore, there have been many direct measurements of the critical line with little or no accompanying VLE data. References 46–52 collectively present critical temperature loci for 95 different binary mixtures, and independent critical density measurements are available for only three of them [20, 53, 54]. Finally, we note that Hicks and Young [55] have comprehensively reviewed the information on binary mixture critical lines through 1973, although many of the mixtures they list have discontinuous critical loci and are therefore not amenable to the present analysis. Critical density (or volume) information is provided for only 91 of a total of 382 mixtures.

Application of the Rainwater–Moldover modification of the Leung–Griffiths model in principle requires the critical density locus as input. It happens that the P–T–x surface is somewhat insensitive to the critical density locus. Hence a fairly accurate coexistence surface in P–T–x can sometimes be constructed based only on a reasonable guess for $\rho_c(x)$, although coexisting densities as predicted by such a model will be entirely speculative. The unfortunate aspect of this lack of sensitivity is that there is apparently no hope of deducing critical densities from P–T–x data alone.

7. FITS OF NONCRITICAL TWO-PHASE ISOCHORES

We now consider the situation in which two-phase isochoric measurements are taken on a binary mixture for which $T_c(x)$ is known but $\rho_c(x)$ is not. The experimentalist can fill a fixed-volume cell with a mixture of known composition at a density which corresponds to the best initial estimate of $\rho_c(x)$ but is not equal to $\rho_c(x)$. The resulting data correspond to noncritical two-phase isochores such as those displayed in Tables I and III. The question then arises whether the mixture critical density can be determined from data along a noncritical isochore.

One approach is suggested immediately by the observations in Section 4. If, to a good approximation, all rectilinear diameters of near-critical isochores lie on the same straight line, we may fit the data to Eq. (19), where $\varepsilon = T - T_c(x)$ and $T_c(x)$ is known, and again set $\rho_c = A/2$.

A second possible approach is to fit such data to Eq. (21), which is based on Eq. (22). This may at first seem inappropriate since, for a noncritical isochore, X_{LV} does not approach $\frac{1}{2}$ as T approaches $T_c(x)$. In fact, X_{LV} abruptly moves toward zero (if $\rho_T < \rho_c$) at the terminus of the isochore. However, Eq. (21) always yields an estimate for ρ_c which "forces" the coexistence densities to yield a value of X_{LV} of $\frac{1}{2}$ in the limit as the critical point is approached [with $\rho_T = \rho_c$ estimated via Eq. (21)]. That this estimated critical density is so close to the model value (see Tables VI and VII described later) has to do somewhat with the nearly coincidental rectilinear diameters at a fixed overall composition. A more detailed theoretical analysis including analysis of experimental data of the type suggested in Section 8 is needed to explain fully why one can fit noncritical isochoric data using Eq. (21) to obtain good estimates of the critical density. These methods are applied to the isochoric results generated by the model for $x_T(N_2) = 0.5088$.

Each noncritical isochore ($\rho_T/\rho_c = 0.931$, 0.965, 1.035, 1.069) is fit separately. The results for the straight line fits, Eq. (19), and for the liquid volume fraction method, Eq. (21), are shown in Tables IV–VII. Data generated by the model are fit including the critical region (Tables IV and VI) and points removed from critical (Tables V and VII). Both methods prove to be quite successful. As with pure fluids [10], Eqs. (19) and (21)

Table IV. Critical Density Estimates Using the Straight-Line Diameter [Eq. (19)] in the Critical Region, $x_T(N_2) = 0.5088$ and $\rho_c = 11.4330\ \text{kmol} \cdot \text{m}^{-3}$

Temperature range (K)	ρ_T ($\text{kmol} \cdot \text{m}^{-3}$)	ρ_T/ρ_c	$\rho_{c,EST}$ ($\text{kmol} \cdot \text{m}^{-3}$)	$[(\rho_{c,EST} - \rho_T)/\rho_T] \times 100$ (%)	$[(\rho_{c,EST} - \rho_c)/\rho_c] \times 100$ (%)
138.458–159.421	10.6442	0.931	11.4427	7.50	0.085
138.238–158.988	11.0329	0.965	11.4321	3.62	−0.008
137.837–159.045	11.8332	1.035	11.4174	−3.51	−0.136
137.664–158.685	12.2219	1.069	11.4082	−6.66	−0.217

Table V. Critical Density Estimates Using the Straight-Line Diameter [Eq. (19)] Away from the Critical Point, $x_T(N_2) = 0.5088$ and $\rho_c = 11.4330\ \text{kmol} \cdot \text{m}^{-3}$

Temperature range (K)	ρ_T (kmol·m^{-3})	ρ_T/ρ_c	$\rho_{c,EST}$ (kmol·m^{-3})	$[(\rho_{c,EST} - \rho_T)/\rho_T] \times 100$ (%)	$[(\rho_{c,EST} - \rho_c)/\rho_c] \times 100$ (%)
138.458–145.180	10.6442	0.931	11.4204	7.29	−0.110
138.238–144.896	11.0329	0.965	11.4087	3.41	−0.213
137.837–144.377	11.8322	1.035	11.3868	−3.76	−0.404
137.664–144.153	12.2219	1.069	11.3769	−6.91	−0.491

yield similar estimates for ρ_c when data up to the critical point are utilized. The straight-line diameter method yields estimates of ρ_c within about 0.2%, while the liquid volume fraction method yields ρ_c estimates within 0.1%. Equation (21) yields more accurate, consistent results for ρ_c (within 0.1%) when data somewhat removed from the critical point are utilized, although the straight-line diameter remains accurate to 0.5% in the critical density.

Table VI. Critical Density Estimates Using the Critical Liquid Volume Fraction Method [Eq. (21)] in the Critical Region, $x_T(N_2) = 0.5088$ and $\rho_c = 11.4330\ \text{kmol} \cdot \text{m}^{-3}$

Temperature range (K)	ρ_T (kmol·m^{-3})	ρ_T/ρ_c	$\rho_{c,EST}$ (kmol·m^{-3})	$[(\rho_{c,EST} - \rho_T)/\rho_T] \times 100$ (%)	$[(\rho_{c,EST} - \rho_c)/\rho_c] \times 100$ (%)
138.458–159.421	10.6442	0.931	11.4454	7.53	0.108
138.238–158.988	11.0329	0.965	11.4372	3.66	0.037
137.837–159.045	11.8332	1.035	11.4315	−3.39	−0.013
137.664–158.685	12.2219	1.069	11.4316	−6.47	−0.012

Table VII. Critical Density Estimates Using the Critical Liquid Volume Fraction Method [Eq. (21)] Away from the Critical Point, $x_T(N_2) = 0.5088$ and $\rho_c = 11.4330\ \mathrm{kmol \cdot m^{-3}}$

Temperature range (K)	ρ_T (kmol · m^{-3})	ρ_T/ρ_c	$\rho_{c,EST}$ (kmol · m^{-3})	$[(\rho_{c,EST} - \rho_T)/\rho_T] \times 100$ (%)	$[(\rho_{c,EST} - \rho_c)/\rho_c] \times 100$ (%)
138.458–145.180	10.6442	0.931	11.4443	7.52	0.099
138.238–144.896	11.0329	0.965	11.4402	3.69	0.063
137.837–144.377	11.8332	1.035	11.4300	−3.41	−0.026
137.664–144.153	12.2219	1.069	11.4276	−6.50	−0.047

8. A PROPOSED EXPERIMENTAL METHOD

A possible procedure to determine ρ_c experimentally is now given. From a straight-line interpolation or other empirical methods such as that of Chueh and Prausnitz [56], one could obtain an estimate of ρ_c for a given composition. A cell would be then filled such that the overall density is equal to this estimate. The cell should be constructed to minimize expansion or contraction due to changes in pressure or temperature.

As T is increased toward the critical point, pressure, temperature, and saturated liquid and saturated vapor densities are obtained. These data are then fit to Eq. (21) to obtain an estimate of ρ_c. If ρ_c from the fit and ρ_T along which the data were taken are too far apart, the experiment could be repeated by filling the cell at a ρ_T equal to the new estimate for ρ_c. A similar, although perhaps less accurate, procedure based on Eq. (19) could also be tried.

It is noted that the results in Table VII especially indicate that if Eq. (21) is used to obtain an estimate of ρ_c, one could be as much as 7% away from the critical isochore and ~15 K below the critical temperature and still obtain a good estimate for the critical density. This procedure therefore enables experimental avoidance of the region very near critical, where gravity effects make measurement extremely difficult [3, 4].

9. SUMMARY

The Leung–Griffiths model [18], as modified by Rainwater and Moldover [14, 16], has provided for the first time a quantitatively accurate description of binary mixture VLE in the critical region. From this model, the thermodynamic behavior along two-phase isochores, both critical and noncritical, is analyzed. The objective is to develop procedures for the efficient determination of critical density loci when only critical temperature loci are known. The needs for such procedures are well documented.

It is observed that rectilinear diameters of isochores for different overall densities at the same overall composition nearly fall along the same straight line. This observation has been exploited to design a procedure for deducing the mixture critical density from experimental data along an isochore near, but not on, the critical density. Two fitting equations are tested, and it is found that the equation based on Van Poolen's liquid volume fraction analysis [8–11] yields the best results.

The modified Leung–Griffiths model at present incorporates only simple scaling, but efforts have commenced to include revised and extended scaling and, therefore, "hooks" in the rectilinear diameters. When this advanced model has been fully developed, the present analysis should be repeated.

Other applications of the method are worth investigating. For example, the critical two-phase isochores might be a convenient replacement for lines of constant ζ as a thermodynamic coordinate in an alternative correlation of the binary mixture coexistence surface. This approach is currently being investigated by Van Poolen.

NOTE ADDED IN PROOF

A thorough measurement of the near-critical VLE surface of ethylene + propylene (see Sec. 5) has recently been published by H. Kubota, H. Inatome, Y. Tanaka and T. Makita, *J. Chem. Eng. Japan* **16**:99 (1983); see also H. Bae, K. Nagahama and M. Hirata, *J. Chem. Eng. Japan* **14**:1 (1981).

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