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Determination of Critical Exponents from Measurements of Binary Vapor-Liquid Equilibrium in the Neighborhood of the Critical Line*

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The shape of the coexistence curve for a binary vapor-liquid equilibria along several isotherms has been found to be described by $(y - x) = c(P_c \text{ mix} - P)^{\beta}$, where y and x are the concentrations of the more volatile component in the vapor and liquid phases, respectively; P_c mix is the critical pressure of the isotherm; P is the pressure; and c is a proportionality constant. A value of $\beta = 1/3 \pm 0.05$ describes the data of the methane-ethane and methane-propane systems from the critical point of methane to 23 °K higher for pressures within 10 psi of the critical pressure of the isotherm. The proportionality constant c appears to have a generalized linear temperature dependence applicable to both systems. The behavior of the heavier component from 1.35 °K above the more volatile (methane) component critical temperature to at least 9 °K higher is mathematically represented by the same type of exponential function for a much wider pressure range of approximately 300 psi.

I. THE DEVELOPMENT OF THE INVESTIGATION

Vapor-liquid equilibria, especially at low temperature, have been investigated for some time [1, 2] at this laboratory. Experimental errors have decreased significantly as improvements in apparatus and techniques developed. A recent investigation [3] covered the −60° to −143°C range for the light hydrocarbon binaries, methane-ethane and methane-propane. The increased precision of the experimental method exposed interesting phenomena about the critical temperature of methane, the more volatile component. Discussion of this behavior [4] revealed that intensive precise investigation was justified for critical exponent evaluation. A brief report of the effects in the critical region has been made [5].

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II. THEORY OF THE CRITICAL REGION

Critical phenomena have been studied on many different physico-chemical properties in fluid, magnetic, and other equilibrium systems. A recent review [6] of equilibrium critical phenomena discussed the principal theoretical aspects and presented special emphasis on the critical exponents. This work was complemented by a review [7] of experimental investigations in the critical region, such as the vapor-liquid critical point of a pure component, the binary liquid-liquid coexistence curve, critical opalescence, magnetic systems, superfluidity, and specific heat. A generalized mathematical treatment is possible for all these properties.

A. *Definition of the Critical Exponent*

In the critical region a sharp change in a physical property often occurs, which either diverges to infinity or converges to zero as a variable (temperature, pressure, *etc.*) approaches its critical point value. Such a singularity can best be described by the exponential function [6]

$$\lim_{x\to 0}\left[\frac{\ln f(x)}{\ln x}\right] = \lambda, \tag{1}$$

where λ is a constant termed the critical exponent, and $f(x)$ is a positive function for $x \to 0+$ and/or for $x \to 0-$. The function $f(x)$ is generally discontinuous at $x = 0$ and the numerical coefficients differ for the two cases. The evaluation of many sets of experimental data in the neighborhood of the critical has shown that this function is suitable [7]; for a more complete discussion and evaluation of the theoretical appropriateness of Eq. (1), see Refs. [6, 7, 8, 9].

B. *Application of Critical Exponents to Fluid Systems*

The coexistence curve for a one-component system. Since the difference between the densities of the two phases is vanishing along the coexistence curve as the temperature approaches the critical temperature, the critical exponent β is defined from Eq. (1) as

$$\rho_v - \rho_l = k \mid T - T_c \mid^{\beta}, \tag{2}$$

where ρ_l and ρ_v are the liquid- and vapor-phase densities, respectively, k is a proportionality constant, T_c is the critical temperature, and T is the equilibrium temperature of the measurement. Some data of densities of coexisting phases for six one-component fluid systems were evaluated by Heller [7] to give the critical exponent β in the range of 0.34 to 0.45 with an average value of $\beta = 0.35$. These observed values are in close agreement with the commonly used $\beta = 1/3$ according to the "cube-root law" known for over 70 years [10].

The coexistence curve for a binary system. The coexistence curves for equilibrium systems of two liquid phases which become completely miscible at a critical (consolute) temperature have been under investigation. If the density of the mixture is assumed proportional to the mole fraction of one of the components, the expression analogous to Eq. (2) is

$$x_1' - x_1'' = k \mid T - T_c \mid^{\beta}, \tag{3}$$

for $T \rightarrow T_c-$, where x_1' and x'' are the mole fractions of component $\underline{1}$ in the two coexisting liquid phases denoted as $'$ and $''$, respectively, k and β are not generally identical with those in Eq. (2), and T_c is the consolute temperature. For example, for the system perfluromethylcyclohexane and carbon tetrachloride investigated by Loven and Rice [11], Thompson and Rice's analysis [12] gave $\beta = 0.335$, while Heller's evaluation [7] gave $\beta = 0.38$.

Vapor-liquid and liquid-liquid phase separations have no essential differences, since the separation is based on the same phenomenological description. However, no previous experimental binary vapor-liquid equilibrium data were measured sufficiently close to the critical separation point to apply Eq. (2) or (3).

We have measured concentrations in the vapor and liquid phases of two binary mixtures as a function of pressure at constant temperature along several isotherms. For these binary systems there is a line of critical points on a P, T, x thermodynamic surface which connects the pure fluid critical points of the two constituents. If P_c mix is the critical pressure at some temperature T (between the two pure fluid critical temperatures), then the distance along the coexistence curve from that critical point is measured by ($P_c$mix $- P$) along the isotherm T. Since the shape of the coexistence curve is characterized asymptotically by the critical exponent β (at either constant pressure or constant temperature [9, 13]), then along the coexistence curve at constant temperature

$$y_1 - x_1 = c(P_c \,\text{mix} - P)^{\beta}, \tag{4}$$

where y_1 is the concentration of component 1 in the vapor phase. For the two systems discussed here, both the liquid and vapor phases are mostly methane, the more volatile component, and y_1 is greater than x_1.

Since the critical exponent β has approximately the same 1/3 value [13] both for the one-component vapor-liquid equilibrium system, Eq. (2), and for the binary liquid-liquid system, Eq. (3), the same value seems probable also for the binary vapor-liquid equilibrium system, Eq. (4).

The critical exponent and proportionality constant in Eq. (2) and (3) have fairly generalized values. Analogously, the constant c in Eq. (4) may exhibit a similar generalized behavior as some function of temperature.

III. EXPERIMENTAL INVESTIGATION

A. *Apparatus*

The details of the experimental equipment are available [2, 3, 14]. An equilibrium cell suitable for visual observations was maintained in a constant temperature bath (±0.01°C), and several small vapor and liquid samples were analyzed at each pressure by gas chromatography to an accuracy of 1% in the peak area ratio; which yielded mole fraction errors of 0.99900 ± 0.00001, 0.9900 ± 0.0001, and 0.900 ± 0.0008.

B. *Method*

An isothermal run started at a low pressure *ca.* 30 psia and continued at increased pressures until the critical pressure at that temperature was reached. The size of the pressure intervals varied with the temperature, but the interval became smaller as the critical condition was approached.

C. *Chronology*

The data reported elsewhere [3, 14] which led to this study had a pressure uncertainty of 2 psi in the region of the methane critical point. After investigation of the methane-ethane-propane ternary system [3, 15], the pressure gage was replaced by a fused quartz precision pressure gage to improve the measurement of (P_c mix $- P$) to ±0.1 psi. The results presented in Table I were obtained over two months after the earlier measurements. The figures clearly indicate that the two data sets are consistent.

D. *Inherent Experimental Difficulties*

The direct measurement of any "equilibrium" property has many obvious difficulties, which arise directly from the perturbation resulting from making any measurement. For this particular investigation and equipment, measurements are taken of temperature, pressure, and composition of each phase. Temperature was controlled within ±0.01°C and was measured by a certified platinum resistance thermometer. The pressure was established by the charging of the cell, and it was measured after equilibrium was attained to a relative accuracy of 0.1 psi. Even with the more sensitive gage, the absolute accuracy of the critical pressure remains larger due to the difficulty of obtaining a critical state in the equilibrium cell. The error in the mole fraction determination was reduced by repeating the sample analysis at least 6 to 10 times for each phase. The sample size was *ca.* 0.2 ml from a total volume *ca.* 100 ml, which did not affect the equilibrium.

TABLE I

Isothermal Vapor-Liquid Equilibrium Data for the Methane-Ethane System Immediately Above the Critical of Methane

CH_4 Mole Fraction		Pressure	K-Value	
x	y	(psia)	Methane	Ethane
Temperature: 191.20 °K				
0.98697	0.99427	663.0	1.0074	0.4398
0.99116	0.99576	668.6	1.0046	0.4796
0.99230	0.99639	670.5	1.0041	0.4688
0.99372	0.99699	672.3	1.0033	0.4793
0.99460	0.99667	673.5	1.0021	0.6167
0.99653	critical	674.2	1.0000	1.0000
Temperature: 193.37 °K				
0.94529	0.97942	647.8	1.0361	0.3762
0.96051	0.98249	665.5	1.0229	0.4434
0.96858	0.98411	676.3	1.0160	0.5057
0.97473	0.98519	683.7	1.0107	0.5861
0.97763	0.98566	687.5	1.0082	0.6410
0.98051	0.98562	691.2	1.0052	0.7378
0.98593	critical	692.7	1.0000	1.0000
Temperature: 194.61 °K				
0.92430	0.97421	646.9	1.0540	0.3407
0.94259	0.97622	665.5	1.0357	0.4142
0.95614	0.97896	682.4	1.0239	0.4797
0.96463	0.98014	692.8	1.0161	0.5615
0.96814	0.98002	697.9	1.0123	0.6271
0.97178	0.98049	701.4	1.0090	0.6914
0.97276	0.97981	702.6	1.0072	0.7412
0.97930	critical	704.0	1.0000	1.0000
Temperature: 197.21 °K				
0.94271	0.97009	712.8	1.0290	0.5221
0.94758	0.96868	719.0	1.0223	0.5975
0.94882	0.96828	720.8	1.0205	0.6198
0.95364	0.96798	724.7	1.0150	0.6907
0.95459	0.96648	726.0	1.0125	0.7382
0.96531	critical	728.3	1.0000	1.0000

E. *Error Analysis*

The maximum error in the equilibrium ratio of the vapor to liquid compositions, or K-value, defined by

$$K = y/x, \tag{5}$$

is the sum of errors from temperature, pressure, and concentration measurements. For the light component, methane, the maximum total error of these measurements is approximately 0.12 %, and for the heavy component, ethane, the maximum total error is 2.7 %. These values were obtained from the same detailed error analysis [3] of the earlier data, which had larger errors. The errors due to concentration were 0.1 % and 2.0 %, respectively. When considerations are made for the multiple analyses and the consistency of these data with the earlier data, evident in Fig. 2, more realistic maximum errors in K are 0.05 % and 1.5 % for the data in Table I.

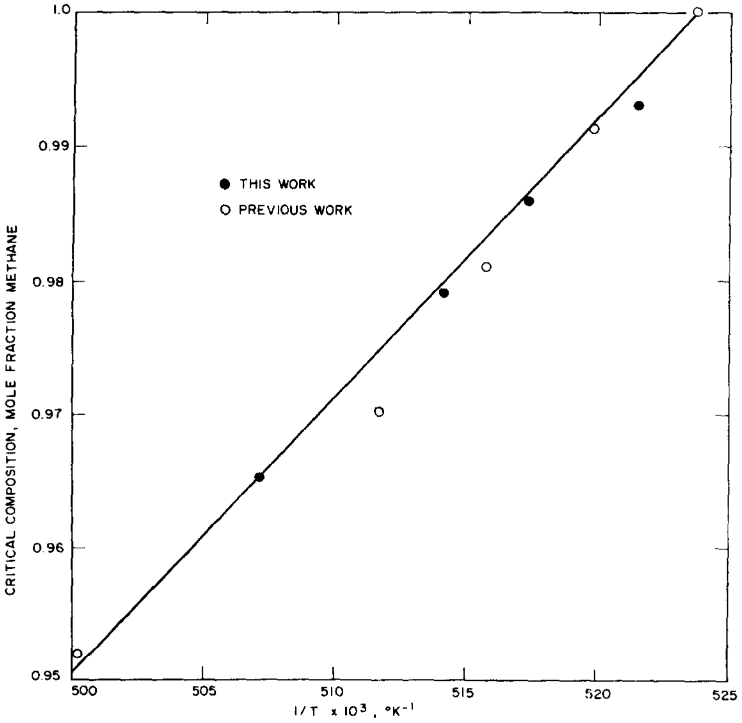

FIG. 1. Methane-Ethane System from T_c of Methane to $T_c + 9°K$

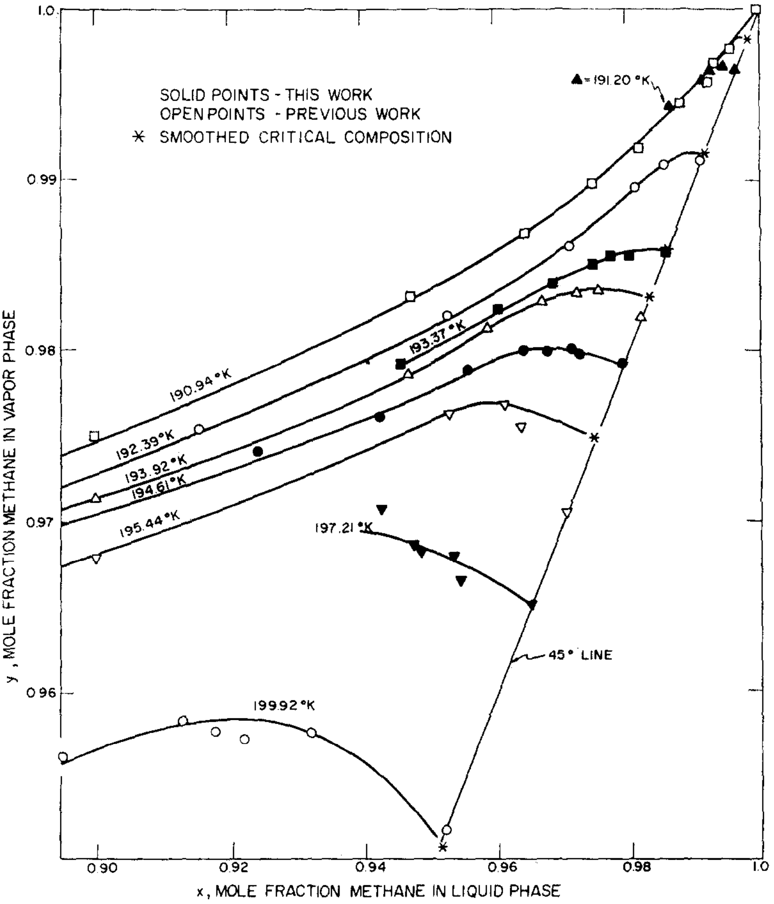

FIG. 2. Methane-Ethane System. Vapor-Liquid Isotherms at T_c of Methane and Higher.

IV. EVALUATION OF EXPERIMENTAL DATA

The data presented here were extensively compared with the data of the earlier work [3, 14] to test the error analysis. Fig. 1 shows the critical composition, the variable of highest error, as a function of reciprocal absolute temperature, the variable of lowest error. It is evident that the critical compositions for the 191.20°K (reported here) and the 195.44°K [3] isotherms are significantly in error. Figure 2 shows the *y vs. x* behavior of the isotherms with the critical compositions from Fig. 1.

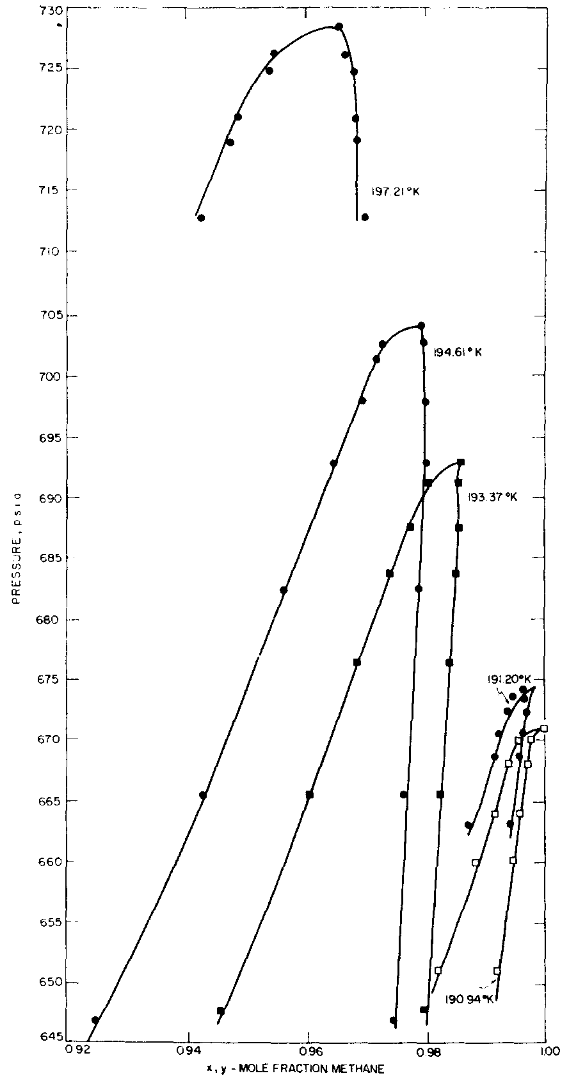

FIG. 3. Methane-Ethane Equilibrium Just above Critical of Methane

A plot of the logarithm of the critical pressure against the reciprocal absolute temperature gave a smoothed line through the data of Table I and "better" values of pressure for the older work. Table II presents smoothed critical compositions and pressures. Figure 3 gives the experimental values for composition with smoothed curves against pressure.

TABLE II

Smoothed Critical Values for the Methane-Ethane System

		Methane	Critical Pressure (psia)	
T, °K	T_c mix − $T_c(CH_4)$	x_c	Smoothed	Experimental
190.94	0.0	1.0000	672.1	671.
191.20	0.26	0.99851	674.2	674.2
192.39	1.45	0.99179	684.4	685.
193.37	2.43	0.98634	692.7	692.7
193.92	2.98	0.98330	697.8	698.
194.61	3.67	0.97948	704.0	704.0
195.44	4.50	0.97498	712.1	713.
197.21	6.27	0.96540	728.3	728.3
199.92	8.98	0.95118	749.6	748.

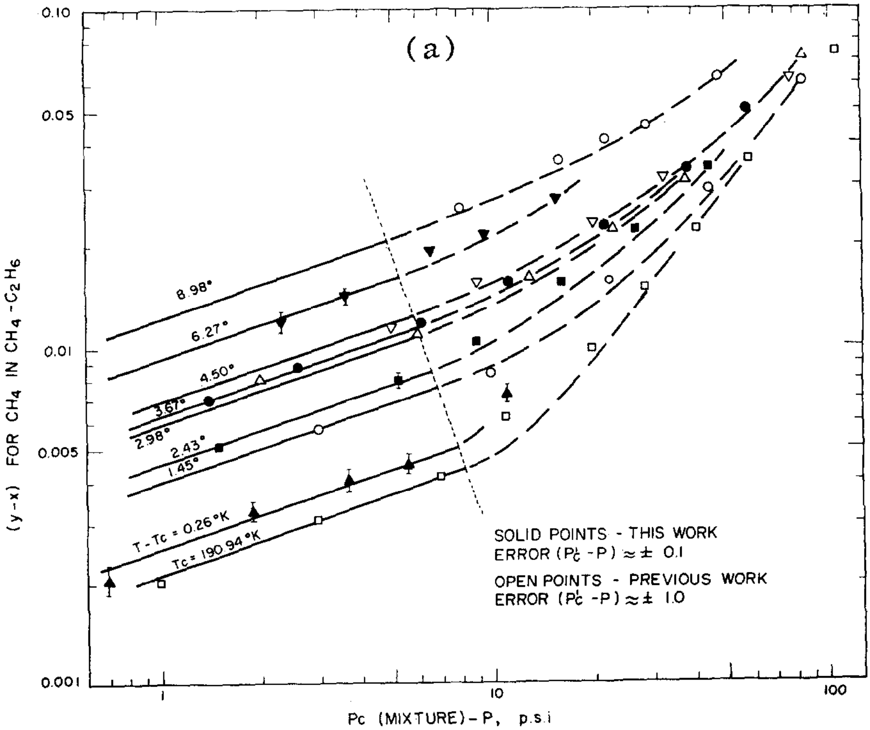

FIG. 4a. Behavior of Methane ($y - x$) at and Just Above Methane Critical in Methane-Ethane System.

The values for the 191.20°K isotherm, only 0.26° from the critical, appear to have errors which exceed the error analysis. This is not surprising, since this is the region of maximum experimental difficulty to achieve and measure equilibrium. Suitable design modifications are needed for better measurements in this region.

V. EVALUATION OF β

The data presented in Table I and the earlier data are presented in Figure 4a according to Eq. (6). Some earlier evaluations were made in terms of $(K-1)$, which are presented in Fig. 4b. On both figures some points have experimental error indicated for $(K-1)$ and $(y-x)$, but the error in the pressure difference is not shown for the earlier data. It is evident that both figures exhibit identical behavior below (P_c mix $-$ P) of 10 psi. The linear portion of the curves, below the dotted lines, have been drawn with the slope β equal to 1/3; all of the data follow this behavior within the experimental errors.

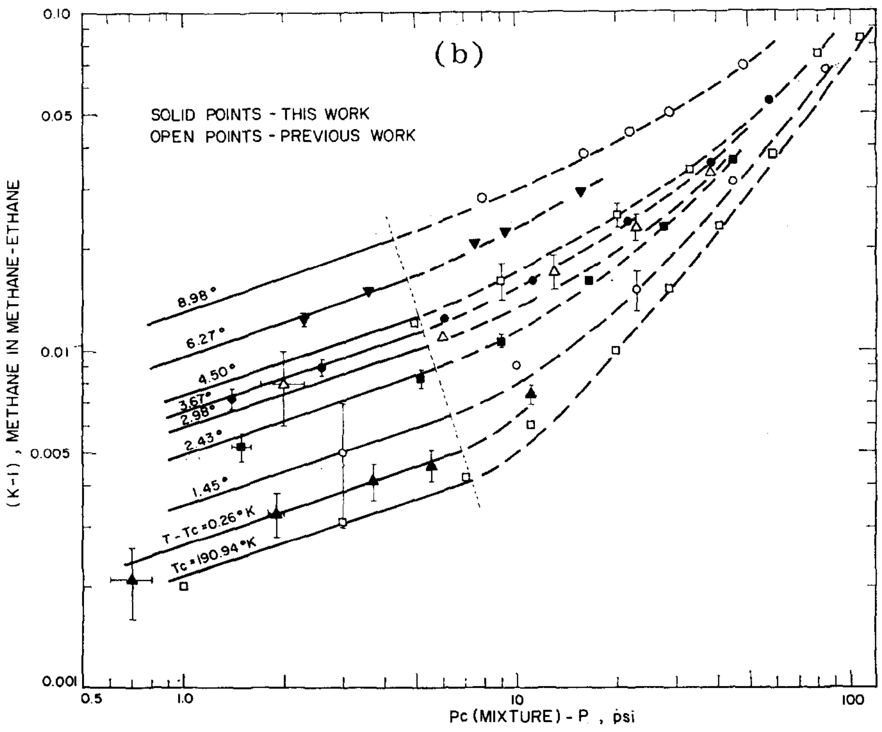

FIG. 4b. Behavior of Methane K at and Just Above Methane Critical in CH_4–C_2H_6 System.

The position of the dotted line is arbitrary and serves to indicate an approximate region where the asymptotic approach to a 1/3 slope is evident. It is quite apparent that only a part of this data and the previous work [14] is in the region of near-critical behavior; however, the trend towards an asymptotic value of $\beta =/ 13$ seems evident. The data [14] even further removed from the critical point (more than 100 psi) show a slope of *ca.* 4/3 for $(K - 1)$. The data of Fig. 4 do not follow a 4/3 behavior. Let us emphasize that these are preliminary results, since few data exist for binary vapor-liquid equilibria near the critical region.

The proportionality constant c, or the intercept at $(P_c \text{ mix} - P)$ equals 1, is shown in Fig. 5a and 5b, as a function of the difference between the temperature of the data and the critical temperature of methane. Similar results are obtained for c *vs.* the ratio of the absolute temperatures, T/T_c methane. The points shown for the less accurate methane-propane system indicate that the constant c could have a generalized value, similar to the one-component system [7]. Unfortunately, there are not sufficient other data available to evaluate this assumption at the present time. The results are identical, since

$$(K - 1) = y/x - 1 = (y - x)/x, \tag{6}$$

$$\ln(K - 1) = \ln(y - x) - \ln x. \tag{7}$$

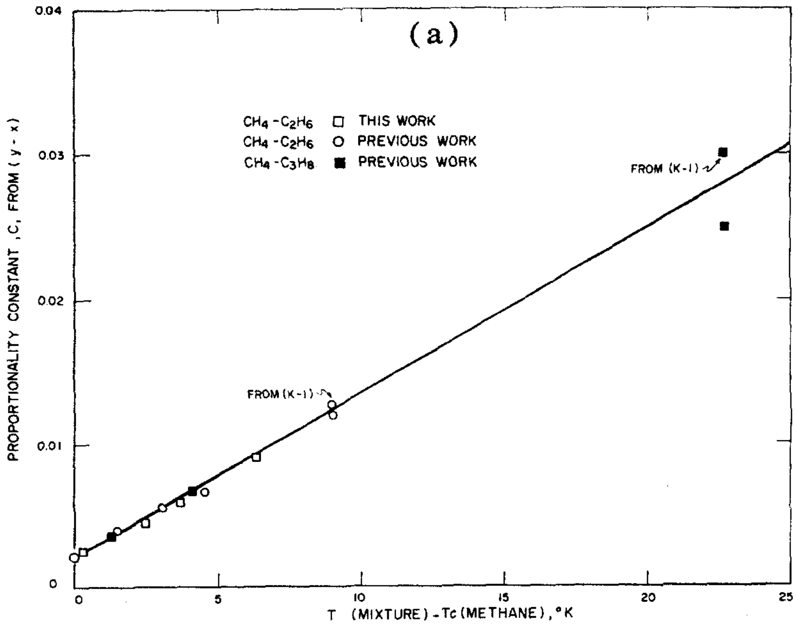

FIG. 5a. Behavior of Methane Proportionality Constant for CH_4–C_2H_6 and CH_4–C_3H_8 Systems from Mole Fraction Difference.

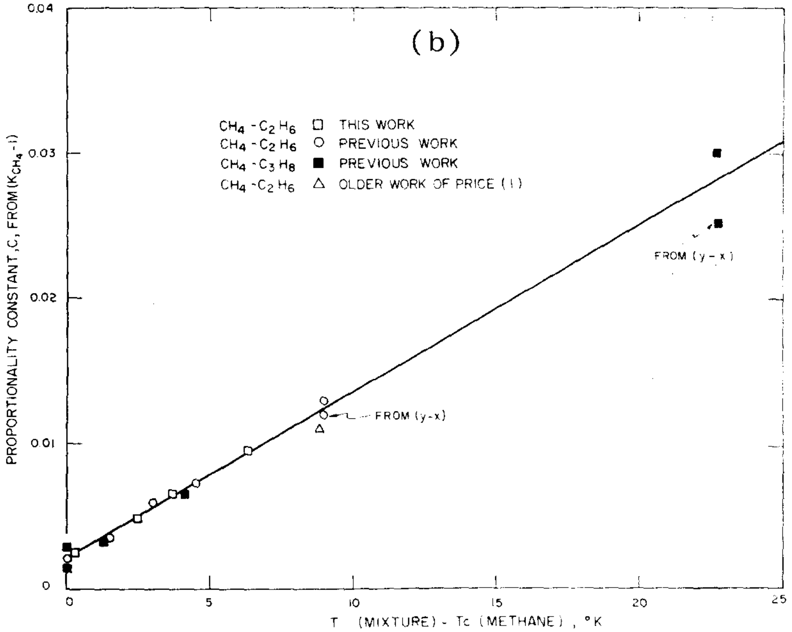

FIG. 5b. Behavior of Methane Proportionality constant for CH_4–C_2H_6 and CH_4–C_3H_8 Systems from $(K_{CH_4} - 1)$.

The data in Table I show that $x \to 1$ as $(P_c \text{ mix} - P) \to 1$; therefore, $\ln x \to 0$ and Eq. (7) approaches Eq. (4). However, as the pressure difference increases, the liquid mole fraction decreases and the second term of Eq. (7) contributes to the behavior of $\ln(K - 1)$.

Shown on the figures are some other values estimated from the methane-propane data [3, 14]; although only three points of these data were below $(P_c \text{ mix} - P)$ of 10 psi. The system evidenced similar behavior at the higher pressure differences for $\ln(K - 1)$.

VI. AN UNEXPLAINED OBSERVATION

From a suggestion of Professor Salsburg [4] that the heavier component behavior should be examined, a plot was made for $\ln(1 - K_2)$ *vs.* $\ln(P_c \text{ mix} - P)$ of the data in Table I. The data for the three higher temperatures, 2.42° to 6.26° above the methane critical temperature, are described by

$$(1 - K_2) = 0.235(P_c \text{ mix} - P)^{0.248}. \tag{8}$$

The older ethane data, except for the critical isotherm, also show similar behavior up to a pressure difference of 200 to 300 psi. The propane data for the methane-propane system showed similar behavior. In terms of the mole fraction of methane, we have

$$(1 - K_2) = 1 - (1 - y)/(1 - x), \tag{9}$$

$$\ln(1 - K_2) = \ln(y - x) - \ln(1 - x). \tag{10}$$

Equation (10) compares to Eq. (7).

The data at the critical isotherm and the 191.20°K isotherm were different, with a small positive slope, estimated as 0.077 for the methane-ethane critical isotherm on a log-log plot. The slope of the methane-propane critical isotherm was estimated to be 0.084. *See note added in proof after Refs.*

VII. DISCUSSION AND CONCLUSIONS

A. *Critical Point of Methane*

Reported values for the critical temperature and pressure vary over 0.56°K and 6.7 psi, as shown by Table III. In this work the apparent methane critical temperature was 190.94°K, and the critical pressure of 671 psia [16] was adopted. However, the smoothed data presented in Table II show that the critical pressure for 190.94°K is 672.1 psia. The smooth line for this data passes through the critical value of Vennix, within the experimental error of these measurements. Hence the

TABLE III

Some Literature Values for the Critical Point of Methane[a]

% Purity	Year	Reference	T_c (°K)	P_c atm	P_c psia	V_c or ρ_c
99.8[b]	1922	[17]	191.03 191.04[c]	45.8	673.	6.2 cc/gm
99.97	1952	[18]	190.55 ± 0.06 190.54[c]	45.47 ± 0.2	668.2	0.1625 gm/cc
99.99+	1970	[16]	190.77	45.66	671.0	
99.99+	1970	[19]	190.498 ± 0.003	45.346 ± 0.01	666.40	99.546 cc/gm mole

[a] A review of other data is available [20], which also notes the wide range of reported values.

[b] Limit of measurement of apparatus. Authors state that they think the purity is higher.

[c] Adjusted to zero of 273.15°.

critical temperature of methane reported here in Table II and Fig. 4 may be 0.2° too high. This apparatus was not originally [2, 3] designed for high precision in the exact determination of the critical point. The change of the pressure gage for the data reported here increased the precision of the value of the difference from the critical pressure of the mixture.

B. *Evaluation of Critical Exponent and Proportionality Constant*

The data of this investigation together with the results of the earlier work [3, 14] indicate that $\beta = 1/3$ with an estimated uncertainty of ± 0.05. This value of β with a proportionality constant c describes isothermal vapor-liquid equilibria of the methane-ethane binary system from the critical temperature of the more volatile component up to 23°K higher for pressures within 10 psi of the critical pressure of the isotherm. The proportionality constant is a linear function of the temperature difference from the critical temperature of the more volatile component and appears to be independent of the system.

Less accurate and not so closely measured data on the methane-propane system show the same behavior as the methane-ethane system and give the same value of proportionality constant c with extrapolation over one order. For complete verification, other systems should be investigated in this region and in the pressures just below the critical pressure of the more volatile component. The behavior of the heavier component from 1.35 to at least 8.98°K above the critical temperature of the more volatile component is evidently uniform from a pressure of about 300 psi below the critical pressure.

C. *Future Work*

The behavior reported here deserves a complete theoretical analysis similar to [8]. Additional experimental data on binary vapor-liquid systems at equilibrium are needed in this region; such experiments would require carefully designed apparatus. It is especially interesting to note that the value of the exponent indicates non-classical behavior. The behavior of the heavier component, expressed in Eq. (10), is especially interesting, since this component is present in relatively small quantities, about 10% and less in the liquid phase, with even smaller amounts in the vapor phase.

ACKNOWLEDGMENTS

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Note added in proof: Professor Griffiths pointed out that $1 - K_2 = (x_2 - y_2)/x_2$ since x_2 goes to a non-zero constant at the critical pressure, this must have the same $\beta(1/3)$ *for sufficiently small* $P_c - P$.

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Note: Theses and Monograph (References 1, 2, 3, 16) are available from University Microfilms, Ann Arbor, Michigan.