Saturated Liquid Densities for Binary Hydrocarbon Systems

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The extension of the rules proposed by Cailletet and Mathias for the sum of the saturated vapor and liquid densities and by Guggenheim for the difference of these densities enabled the development of a method for the prediction of liquid densities for binary hydrocarbon systems at saturated conditions. The theorem by corresponding states indicated that unique relationships should exist between the reduced temperature and the sum and difference of the reduced saturated liquid density and the reduced saturated vapor density.

Density data reported by Kay for the systems *n*-butane—*n*-heptane, ethane—*n*-butane, ethane—*n*-heptane, and ethane—cyclohexane were used to determine the exponents and the coefficients of the resulting equations. The exponents were found to be functions of two temperature parameters, which take into account both the components and composition of the mixture, while their coefficients have been found to depend only on their exponents.

It has been previously shown that critical temperatures of binary hydrocarbon systems can be predicted with the two temperature parameters. In this study it has been found that these two parameters can also be applied to determine the critical densities for these binary hydrocarbon systems. Using these critical properties one can directly obtain the saturated liquid densities of binary systems from the two reduced-density relationships.

The method developed in this work reproduces the saturated liquid densities of the four systems within 4.8%. In addition saturated densities have been calculated for the ethylene—*n*-heptane system and checked the experimental values within 3.2%.

Because saturated vapor densities are small compared with the saturated liquid densities for conditions removed from the critical point, the sum and difference of the liquid and vapor densities are approximately the same. Thus this method cannot be used with any reliability to determine the densities of saturated vapors.

At present this method can be applied only to hydrocarbon mixtures whose atmospheric dew point does not exceed twice its atmospheric boiling point.

Considerable information has been presented in the literature for the estimation of densities of pure substances. A number of compressibility factor correlations has been developed to account for the gaseous PVT-behavior of pure substances (*12, 13, 14, 16*). In 1943 Watson (*19*) presented an analysis for the liquid state in which the liquid density is related to the ω-factor. Lydersen, Greenkorn, and Hougen (*12*) introduced the critical compressibility factor z_c as a third correlating parameter to develop reduced-density correlations which apply both to gaseous and liquid states of pure substances. Largely owing to this work and the work of Pitzer (*14*), who introduced the acentric factor, the PVT-behavior of pure substances is well defined. However the PVT-behavior of mixtures is a more complex problem, primarily because of the interaction of unlike molecules.

Idealized cases can be treated by the use of additive volumes. To determine the PVT-behavior of real mixtures the pseudocritical concepts proposed by Kay (*6*) and Joffe (*5*) can be applied. Recent activity in work concerning mixtures is reported by Prausnitz and Gunn (*15*), who utilized the second virial coefficient to calculate pseudocritical constants. Steward et al. (*18*) utilized pseudocritical constants and the reduced density correlations of Lydersen, Greenkorn, and Hougen (*12*) to obtain densities of mixtures in the gaseous and liquid states removed from saturation conditions.

Despite the efforts of these various investigators no method has been developed to treat the saturated gaseous and liquid states of mixtures, particularly in the vicinity of the critical point. For hydrocarbon binary systems comprehensive information is available from the work of Kay. Representative systems from his work (*7, 8, 9, 11*) including mixtures of *n*-butane and *n*-heptane, ethane and *n*-butane, ethane and *n*-heptane, and ethane and cyclohexane were arbitrarily selected and were used to establish the PVT-behavior of binary mixtures in their saturated state.

BEHAVIOR OF BINARY HYDROCARBON SYSTEMS

The densities of multicomponent systems at saturated conditions exhibit a very unusual behavior. The density data for the saturated liquid and vapor states are presented in Figures

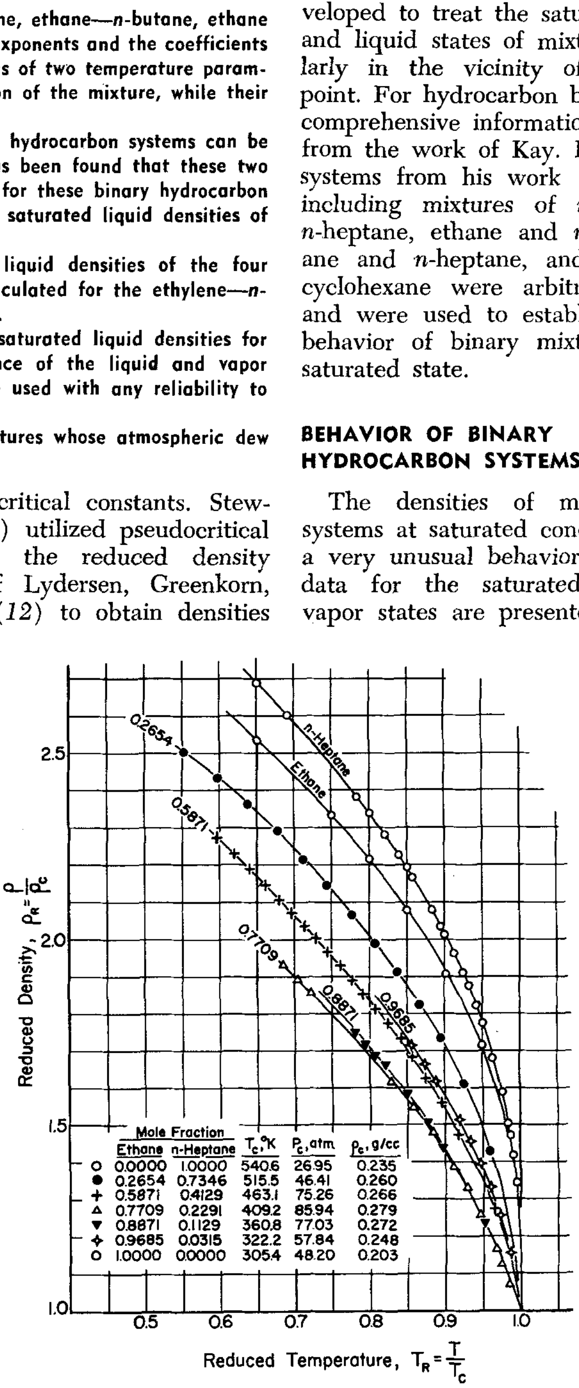

Fig. 1. Saturated liquid densities of several compositions of the ethane-*n*-heptane system.

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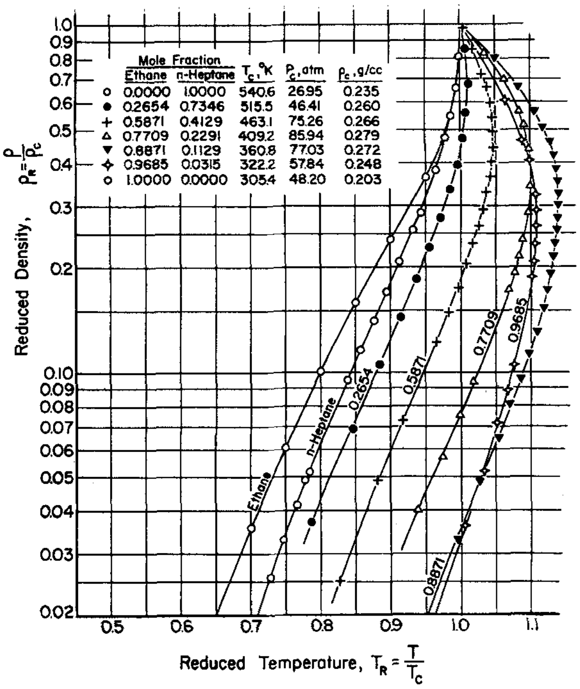

Fig. 2. Saturated vapor densities of several compositions of the ethane-n-heptane system.

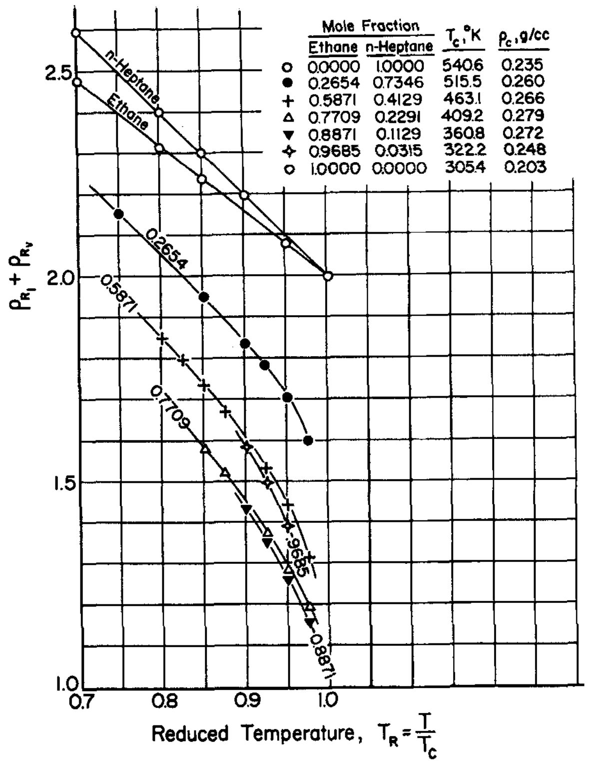

Fig. 3. Rectilinear diameter plot for different compositions of the ethane-n-heptane system.

1 and 2 for the system ethane—*n*-heptane (*7*). In these figures reduced density is related to reduced temperature. These reduced values were obtained from the reported experimental densities and temperatures and the corresponding critical constants for each composition. To indicate the effect of composition on density the densities of pure ethane and *n*-heptane are also included in these figures.

These density curves show that for a given temperature the density of *n*-heptane decreases with increasing ethane content until a minimum is reached, after which the density increases and approaches that of pure ethane. Similar behavior was exhibited by the other systems investigated in this study. In contrast to the regular behavior of pure substances, mixtures possess saturated density envelopes which exhibit maximum temperatures for the gaseous state above $T_R = 1.0$. This phenomenon becomes more pronounced for compositions containing a large proportion of the more volatile component. Furthermore it is readily obvious from Figure 2 that both the variation of density with composition at a given temperature and the point of maximum temperature increase as the difference between the molecular weights of the components of the mixture increases. This behavior is closely related to retrograde condensation effects.

This unusual density variation has prevented the development of density relationships for mixtures in the vicinity of the critical point. A review of the dependence of density on temperature presented in Figures 1 and 2 indicates that rigorous studies are extremely complicated. In order to minimize the complexity of this problem and at the same time establish a method that possesses some degree of reliability and practicality, an empirical approach has been employed that utilized the properties of the mixtures to define parameters that are specific to a particular composition.

TREATMENT OF EXPERIMENTAL DATA

The rectilinear diameter rule of Cailletet and Mathias (*1*) for the determination of densities of pure substances in the saturated liquid and vapor states indicates that a linear relationship which passes through the critical point should exist between the sum of the saturated densities and temperature. A critical survey of pure ethane showed that the data of Kay (*7*) and Sage, Webster, and Lacey (*17*) were inconsistent with this rule. Consequently the saturated envelope for ethane in the vicinity of the critical point has been constructed with the data of argon (*4*), which has a critical compressibility factor nearly equal to that of ethane. The resulting densities of ethane were then found to follow the rectilinear diameter rule.

When one applied the rectilinear diameter method to the binary hydrocarbon mixtures considered, the sum $\rho_{R_l} + \rho_{R_v}$ for each mixture was related to the actual reduced temperature. Nonlinear relationships for each mixture were obtained, as shown in Figure 3 for the ethane—*n*-heptane system. As a result the rectilinear diameter rule does not apply directly to mixtures in the vicinity of the critical point. However the general trend of the curves in Figure 3 suggests that these relationships can be linearized by raising $(\rho_{R_l} + \rho_{R_v})$ to some exponent. The exponents were established by a trial-and-error procedure, and the resulting linear relationships are shown in Figure 4. From Figure 4 the slopes and intercepts of each line were used to establish the coefficients a and b in the following equation:

$$(\rho_{R_l} + \rho_{R_v})^m = a\,T_R + b \qquad (1)$$

The values *m*, *a*, and *b* for the ethane—*n*-heptane system are listed in Figure 4, and the corresponding values for the other three hydrocarbon systems are presented in Table 1 along with the actual critical temperatures and critical densities of each mixture.

Guggenheim (*3*) proposed the following relationship for the differences of saturated densities of pure substances:

$$\rho_{R_l} - \rho_{R_v} = \frac{7}{2}\,(1 - T_R)^{1/3} \qquad (2)$$

In order to maintain consistency with the form of Equation (2) the follow-

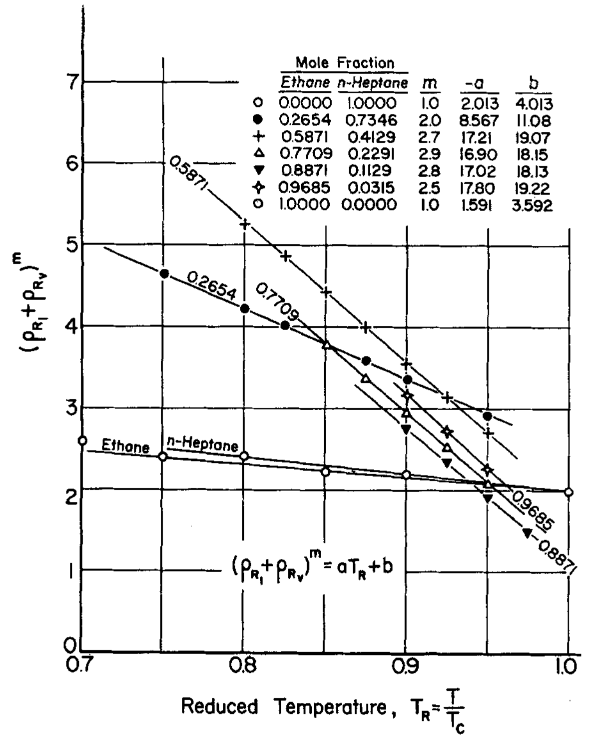

Fig. 4. Extension of the rectilinear diameter rule to mixtures of ethane and *n*-heptane.

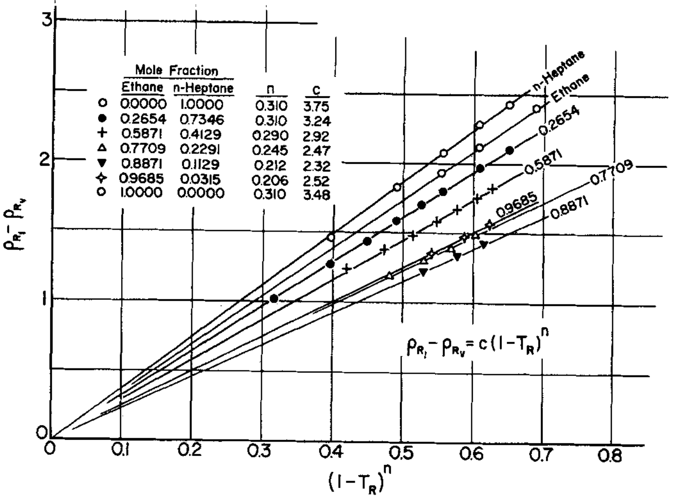

Fig. 5. Relationship of reduced-density difference and reduced temperature for different compositions of the ethane-*n*-heptane system.

ing extension of this equation has been adopted for mixtures:

$$\rho_{R_l} - \rho_{R_v} = c(1 - T_R)^n \qquad (3)$$

By a proper selection of exponent n straight lines passing through the origin were obtained when the density difference $\rho_{R_l} - \rho_{R_v}$ was plotted against the quantity $(1 - T_R)^n$. The relationships resulting for the different compositions of the ethane—*n*-heptane system are presented in Figure 5. The values of c were determined from the slopes of the lines in Figure 5. The respective values of c and n are presented in Figure 5 for the ethane—*n*-heptane system, and the corresponding values for the other three hydrocarbon systems appear in Table 1.

CORRELATION OF EXPONENTS m AND n

It is extremely difficult to correlate exponents m and n with common physical properties of the mixtures by means of a theoretical approach. Because of these complications the exponents m and n have been related to two temperature parameters introduced by Grieves and Thodos (2) to account for the composition and the constituents of multicomponent systems. These parameters have been used for the prediction of actual critical temperatures and critical pressures of binary hydrocarbon systems (2).

The first parameter γ is the ratio at atmospheric pressure of the dew-point temperature to the bubble-point temperature. These temperatures are calculated from vapor-pressure data of the individual components of the mixture. The second temperature parameter is $\vartheta = (T'_b - T_b)/(T_d - T_b)$. For the systems investigated in this study values of γ and ϑ are presented in Table 1.

The relationship between m and the temperature parameters γ and ϑ is presented in Figure 6, in which $m/\gamma^{0.6}$ is shown to be a function of ϑ. Similarly in Figure 7 the exponent n is shown to be dependent on γ for parameters of ϑ.

It was found that the coefficient a in Equation (1) can be directly related to m as follows:

$$a = -1.5\, m^{5/2} \qquad (4)$$

Likewise the coefficient b of Equation (1) was found to be a function of m:

$$b = 3.05\, m^{\frac{15}{8}} \qquad (5)$$

Therefore Equation (1) now becomes

$$\rho_{R_l} + \rho_{R_v} = [3.05\, m^{15/8} - 1.5\, m^{5/2}\, T_R]^{1/m} \qquad (6)$$

For the coefficient c of Equation (3) the following relationship was established:

$$c = 10.9\, n \qquad (7)$$

Thus Equation (3) can be expressed as

$$\rho_{R_l} - \rho_{R_v} = 10.9\, n\, [1 - T_R]^n \qquad (8)$$

Combining Equations (6) and (8) one gets

$$\rho_{R_l} = 1/2\, [3.05\, m^{15/8} - 1.5\, m^{5/2}\, T_R]^{1/m} + 5.45\, n\, [1 - T_R]^n \qquad (9)$$

Thus the reduced density of the saturated liquid mixture can be calculated from the values of m and n obtained

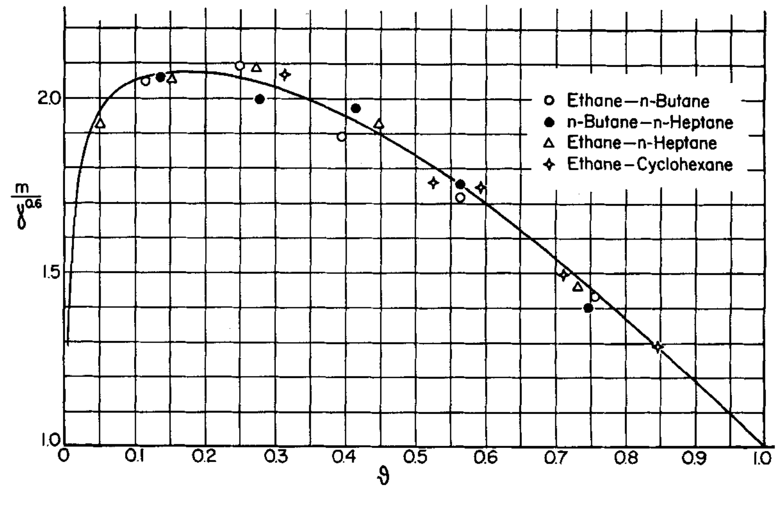

Fig. 6. Relationship of exponent *m* and temperature parameters.

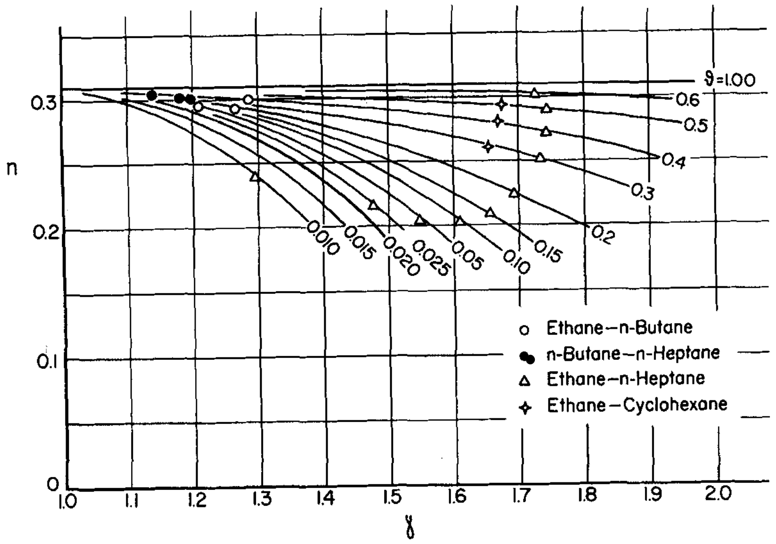

Fig. 7. Relationship of exponent n and temperature modulus γ for different parameters of ϑ.

from Figures 6 and 7 and the actual reduced temperature of the mixture. Equation (9) is essentially a reduced equation of state for the saturated liquid in the vicinity of the critical point for which no other reliable equation has been proposed.

CRITICAL VOLUME

The temperature parameters γ and ϑ have been used to correlate the ratio of the actual molar critical volume to the pseudocritical volume which represents the weighted molar average of the critical volumes of the pure components of the mixture. The actual critical volumes were obtained from the experimental critical densities of each mixture and are presented in Table 1. In Figure 8 the ratio, v_c/v'_c, is shown to be a function of ϑ for constant values of γ.

Example. Determine the liquid density at saturated conditions of a binary mixture of ethane and n-butane consisting of 0.6577 mole fraction of ethane at 188°, 175°, 128°, and 95°F. with the following data:

	T_b, °R.	T_c, °R.	ρ_c, g./cc.
Ethane	331.7	549.8	0.203
n-Butane	491.6	765.7	0.228

Temperature Parameters γ and ϑ and Critical Temperature of Mixture

The boiling point at atmospheric pressure is calculated from the relationship $P_2 x_2 + P_4 x_4 = 14.7$, where P_2 and P_4 represent the vapor pressures of ethane and n-butane, respectively. By trial-and-error, with vapor pressure data, T_b can be found to be 346.6°R.

The dew point at atmospheric pressure is calculated from the relationship $y_2/P_2 + y_4/P_4 = 1/14.7$. Again by trial-and-error the vapor pressures at $T_d = 447.4$°R. satisfy this condition.

The pseudocritical temperature and the pseudonormal boiling point for this mixture thus become

$T'_c = 549.8\ (0.6577) + 765.7\ (0.3423) = 623.7°\text{R.}$

$T'_b = 331.7\ (0.6577) + 491.6\ (0.3423) = 386.5°\ \text{R.}$

From these values γ and ϑ are calculated to be

$$\gamma = \frac{T_d}{T_b} = \frac{447.4}{346.6} = 1.291 \text{ and } \vartheta = \frac{T'_b - T_b}{T_d - T_b}$$

$$= \frac{386.5 - 346.6}{447.4 - 346.6} = 0.396$$

When one uses the method of Grieves and Thodos (2), $T_c/T'_c = 1.047$.

Therefore for this mixture $T_c = 1.047 \times 623.7 = 653.3°\text{R.}$

Critical Density of Mixture

The pseudocritical volume $v_{c_2}\, x_2 + v_{c_4}\, x_4$ of this mixture becomes

$$v'_c = \frac{30.07}{0.203} \times 0.6577 + \frac{58.12}{0.228} \times 0.3423$$

$$= 184.7 \text{ cc./g.-mole}$$

For $\gamma = 1.291$ and $\vartheta = 0.396$, $\dfrac{v_c}{v'_c} = 0.868$ (Figure 8).

Therefore $v_c = 0.868 \times 184.7 = 160.3$ cc./g.-mole.

The critical density of this mixture thus becomes

$$\rho_c = \frac{M}{v_c}$$

$$\frac{0.6577 \times 30.07 + 0.3423 \times 58.12}{160.3}$$

$$= 0.248 \text{ g./cc.}$$

Exponents m and n for Equation (9)

For $\vartheta = 0.396$ the use of Figure 6 produces

$$\frac{m}{\gamma^{0.6}} = 1.955$$

Therefore $m = 1.955\ (1.291)^{0.6} = 2.28$. Also from Figure 7, $n = 0.300$. Substituting these values of m and n into Equation (9) one gets

$$\rho_{R_l} = \tfrac{1}{2}\ [3.05\ (2.28)^{15/8}$$

$$-\ 1.5\ (2.28)^{5/2} T_R]^{1/2.28}$$

$$+\ 5.45\ (0.300)\ [1 - T_R]^{0.300}$$

$$= \tfrac{1}{2}\ [14.34 - 11.78\ T_R]^{0.439}$$

$$+\ 1.64\ [1 - T_R]^{0.300}$$

The values of the saturated liquid densities for each temperature are calculated to be as follows:

t, °F.	T, °R.	T_R	ρ_{R_l}	ρ_l, g./cc. This study	 Kay (8)
188	648	0.992	1.151	0.285	0.266
175	635	0.972	1.357	0.336	0.317
128	588	0.900	1.714	0.425	0.406
98	555	0.850	1.878	0.466	0.446

DISCUSSION OF RESULTS

The method of calculating saturated densities according to the procedure outlined in this study possesses certain

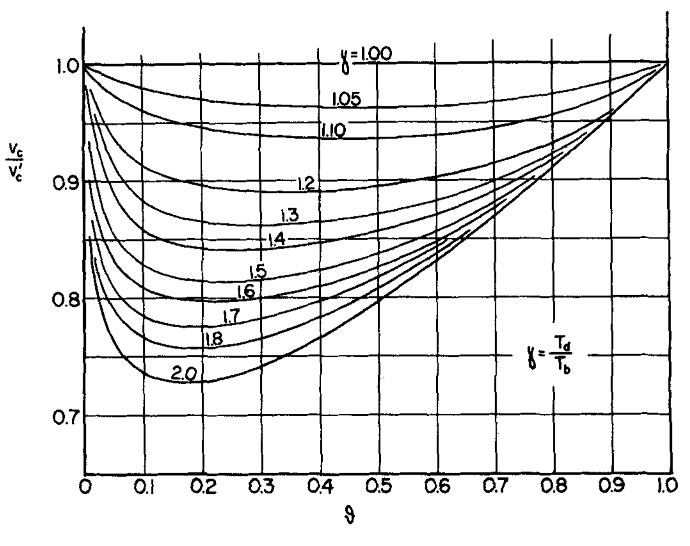

Fig. 8. Variation of critical volume ratio with temperature parameter ϑ.

TABLE 1. DERIVED CONSTANTS OF HYDROCARBON MIXTURES FOR ESTIMATION OF SATURATED LIQUID DENSITY

Ethane—n-butane C_2H_6	 n-C_4H_{10}	T_c, °K.	ρ_c, g./cc.	γ	ϑ	m	$-a$	b	n	c
0.1749	0.8251	412.7	0.238	1.207	0.758	1.6	4.872	7.497	0.310	3.42
0.4510	0.5490	377.3	0.241	1.290	0.563	2.0	8.478	11.15	0.310	3.27
0.6577	0.3423	361.6	0.244	1.291	0.396	2.2	10.60	13.13	0.298	3.13
0.8218	0.1782	337.4	0.235	1.254	0.250	2.4	13.17	15.93	0.290	3.12
0.9472	0.0528	315.6	0.225	1.173	0.114	2.25	11.63	14.75	0.310	3.34
n-butane—*n*-heptane n-C_4H_{10}	 n-C_7H_{16}									
0.1590	0.8410	528.8	0.252	1.124	0.747	1.5	4.396	6.759	0.310	3.46
0.4249	0.5751	504.8	0.261	1.196	0.563	1.95	7.808	10.45	0.305	3.27
0.6311	0.3689	481.9	0.260	1.203	0.414	2.2	10.62	13.30	0.300	3.21
0.8010	0.1990	458.8	0.252	1.176	0.277	2.2	11.49	14.38	0.305	3.30
0.9410	0.0590	436.2	0.240	1.115	0.137	2.2	11.23	14.79	0.310	3.52
Ethane—*n*-heptane C_2H_6	 n-C_7H_{16}									
0.2654	0.7346	515.5	0.260	1.693	0.733	2.0	8.567	11.08	0.310	3.24
0.5871	0.4129	463.1	0.266	1.765	0.447	2.7	17.21	19.07	0.290	2.92
0.7709	0.2291	409.2	0.279	1.734	0.273	2.9	16.90	18.15	0.245	2.47
0.8871	0.1129	360.8	0.272	1.674	0.151	2.8	17.02	18.13	0.212	2.32
0.9685	0.0315	322.2	0.248	1.550	0.050	2.5	17.80	19.22	0.206	2.52
Ethane—cyclohexane C_2H_6	 C_6H_{12}									
0.1378	0.8622	537.4	0.292	1.505	0.847	1.65	4.283	6.791	0.310	3.22
0.2893	0.7107	515.5	0.302	1.623	0.712	2.0	7.905	10.18	0.310	3.04
0.4284	0.5716	489.5	0.314	1.665	0.593	2.35	10.16	12.12	0.310	2.88
0.5020	0.4980	473.8	0.307	1.676	0.526	2.40	12.95	14.58	0.296	2.82
0.7299	0.2701	412.0	0.295	1.660	0.315	2.80	15.96	17.17	0.264	2.55

novel features and some limitations. In this connection densities for the saturated liquid state can be calculated that are within 5% of the actual densities. This deviation follows from a comparison between approximately 160 calculated density values and the experimental values reported by Kay (*7, 8, 9, 10, 11*). In these comparisons besides the investigated systems, the ethylene—*n*-heptane system has been tested for two compositions containing high percentages of ethylene. The calculated results reproduced the experimental data with an average error of 3.2%.

This study applies reasonably well to nonpolar mixtures having a temperature parameter $\gamma < 2.0$. This method has not been applied to hydrocarbon mixtures containing hydrogen and methane, since mixtures containing these components produce a temperature parameter $\gamma > 2.0$ which is beyond the scope of this study.

Although the method of this investigation was developed for binary systems, it should apply to multicomponent systems in general having a temperature parameter $\gamma < 2.0$. Because of the limited experimental density data available for the saturated state of multicomponent systems this extension cannot be confirmed. Nevertheless since binary systems exhibit extreme behavior, the method presented in this investigation should be capable of predicting even more reliably saturated liquid densities of mixtures having more than two components. This method should also be adaptable to include systems having a temperature parameter $\gamma > 2.0$.

NOTATION

a = coefficient for Equation (1)
b = coefficient for Equation (1)
c = coefficient for Equation (3)
m = exponent for Equation (1)
M = molecular weight
n = exponent for Equation (3)
n_i = mole fraction
P_c = critical pressure, atm.
T = temperature, °K.
T_b = normal boiling point of mixture, °K.
T'_b = pseudo normal boiling point of mixture, °K.
T_c = critical temperature of mixture, °K.
T_d = normal dew point of mixture, °K.
T_R = reduced temperature of mixture, T/T_c
v = molar volume of mixture, cc./g.-mole
v_c = critical molar volume of mixture, cc./g.-mole
v'_c = pseudocritical molar volume of mixture, cc./g.-mole
z_c = critical compressibility factor, $P_c v_c / RT_c$

Greek Letters

γ = temperature parameter, T_d/T_b
ϑ = temperature parameter, $(T_b' - T_b)/(T_d - T_b)$
ρ = density, g./cc.
ρ_c = critical density of mixture, g./cc.
ρ_l = density of saturated liquid, g./cc.
ρ_v = density of saturated vapor, g./cc.
ρ_{R_l} = reduced density for saturated liquid, ρ_l/ρ_c
ρ_{R_v} = reduced density for saturated vapor, ρ_v/ρ_c
ω = $\rho T_c / M P_c$

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Manuscript received February 24, 1960; revision received October 3, 1960; paper accepted October 5, 1960.