The Critical Pressures of Multicomponent Hydrocarbon Mixtures and the Critical Densities of Binary Hydrocarbon Mixtures

ROBERT B. GRIEVES and GEORGE THODOS

The Technological Institute, Northwestern University, Evanston, Illinois

A method of predicting the critical pressures of multicomponent hydrocarbon mixtures of known composition has been developed. These mixtures include ternary, quaternary, and quinary systems consisting of normal and isoparaffins, olefins, acetylenes, naphthenes, and aromatics. The method, based upon the mole fraction of the low-boiling component in the mixture, graphically presents the ratio of the actual critical pressure to the pseudocritical pressure as a function of a boiling parameter. For mixtures of more than two components the pseudocritical pressure is based on the critical pressure of the pure low-boiling component and on the actual critical pressure of the mixture consisting of all the remaining higher-boiling components. From an analysis of twenty-seven binary systems (139 compositions) the average deviation of calculated values from reported values is 1.27%. For thirty-four mixtures containing from three to seven components the average deviation is 1.64%.

Based upon a similar approach graphical relationships are presented for the estimation of the critical molar density of binary hydrocarbon mixtures of known composition, which also may contain normal and isoparaffins, olefins, naphthenes, and aromatics. The same boiling point parameter is used to correlate the ratio of the critical density to the reciprocal of the molar average critical volume for nonmethane systems and the product of the critical pressure and the critical volume for methane systems. From an analysis of fifteen binary systems (eighty compositions) the average deviation of calculated values from reported values is 1.54%.

The accurate establishment of the critical state of hydrocarbon mixtures is of importance in many areas of chemical engineering. The critical point represents the limiting condition in vapor-liquid equilibrium studies at which the equilibrium constants of all the components become unity. For a mixture of constant composition it is the point where the bubble and dew point curves meet. It also is of value in assisting the establishment of the P-T phase diagrams for reservoir hydrocarbon fluids and for special synthetic mixtures. Efforts are currently being made to use the actual critical temperature and critical pressure as a basis for reduced state correlations of P-V-T, thermodynamic, and transport properties of mixtures, instead of using the corresponding pseudocritical values. The establishment of the critical density of mixtures is of considerable value for a complete analysis of volumetric and compressibility properties. From the knowledge of the critical temperature, pressure, and density the critical compressibility factor for mixtures may be determined.

A number of accurate methods of calculating the critical temperatures of mixtures have already appeared in the literature. With the methods of Eilerts et al. (*9*), Davis et al. (*7*), Organick (*30*), Kurata and Katz (*23*), Etter and Kay (*11*), and Grieves and Thodos (*14*) the critical temperatures of mixtures containing all types of hydrocarbons, in addition to small amounts of nitrogen and carbon dioxide, may be precisely determined.

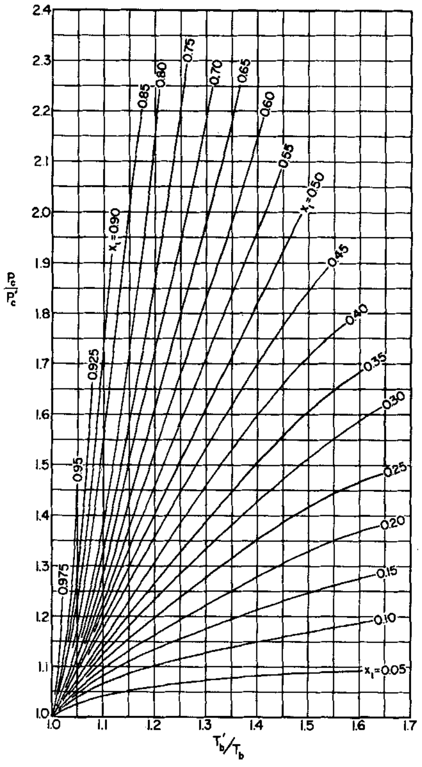

Fig. 1. Relationships between P_c/P'_c and T'_b/T_b for nonmethane hydrocarbon systems.

CRITICAL PRESSURE

A number of correlations for computing the critical pressure of hydrocarbon mixtures have been developed from information obtained by relatively simple means. Those properties of the mixture that can be determined readily, such as composition and pure component properties, are used in the computations. Mayfield (*25*), Eilerts et al. (*9*), Grieves and Thodos (*13*), Kurata and Katz (*23*), Davis et al. (*7*), Smith and Watson (*38*), Organick (*30*), Organick and Brown (*31*), and Etter and Kay (*11*) have presented correlations for the critical pressures of hydrocarbon mixtures of varying complexity.

Most of these methods, although valuable, have certain shortcomings, and consequently there still appears to be a need for a method of determining accurately the critical pressure of mixtures containing as components all types of hydrocarbons, such as paraffins, olefins, acetylenes, naphthenes, and aromatics. Special emphasis should be placed upon ternary, quaternary, and quinary systems and upon systems containing methane, in addition to complex, naturally occurring mixtures. Most of the above methods do not include all types of hydrocarbons and have particular difficulty with methane containing systems.

ESTABLISHMENT OF THE CORRELATION

The relationship permitting the determination of the critical pressure of hydrocarbon mixtures containing two or more components is based on the number of moles of the low-boiling component in the mixture. Since the most accurate and plentiful data in the literature are for binary systems, these provided the starting point for the development. The ratio of the actual critical pressure to the pseudocritical (molar average) pressure P_c/P_c' in two-component systems attained a maximum value at a molar concentration of the low-boiling component, which is always greater than 0.5. This maximum value corresponds to a higher mole fraction of the low-boiling component as the diversity in properties of the pure components increases. In addition for a fixed mole fraction of low-boiling component the critical pressure ratio is an increasing function of the diversity in properties of the pure components.

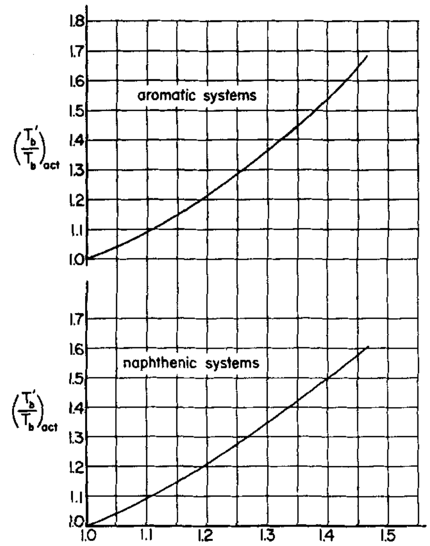

Fig. 2. Relationships between corrected and actual values of the boiling parameter for naphthenic and aromatic systems.

The dimensionless parameter T'_b/T_b was chosen to represent the differences in the properties of the components. T'_b is the molar average of the normal boiling points of the two components; T_b is the boiling point of the mixture at atmospheric pressure calculated from the relationship

$$\pi = 14.7 = P_1x_1 + P_2x_2 \qquad (1)$$

The atmospheric boiling point T_b is arrived at by a trial-and-error procedure. T_b is chosen and the vapor pressures of the components determined; the vapor pressures and mole fraction are then substituted into Equation (1) to see if the equality holds. The approximate straight lines given by a plot of the logarithm of the vapor pressure of each pure component vs. the reciprocal of the absolute temperature are sufficiently accurate for the evaluation of T_b. By use of T'_b/T_b the relationship of the critical pressure of the mixture to that of its pure components is described by the relationship of the vapor pressure behavior of the mixture compared with that of its pure components.

For multicomponent mixtures the number of moles of low-boiling component may again be used to describe the critical pressure behavior. However the pseudocritical pressure P'_c appearing in the ratio P_c/P'_c is no longer the molar average of the critical pressures of the pure components. Instead it is the molar average of the critical pressure of the pure, low-boiling component and of the actual critical pressure of the mixture of the two or more higher boiling components. Thus the effect of all the high-boiling components is reduced to that of a single pseudo component. The parameter T'_b/T_b is evaluated in a manner similar to that for binary systems. T'_b is the molar average of the boiling points of all components, and T_b is evaluated from the relationship

$$\pi = 14.7 = \sum_{i=1}^{n} P_i x_i \qquad (2)$$

where n is the number of components.

NONMETHANE SYSTEMS

Binary Systems

Based upon data in the literature for twenty nonmethane containing binary systems the relationship between the critical pressure ratio P_c/P'_c and the boiling parameter T'_b/T_b is presented as Figure 1. The parameters are the mole fraction of low-boiling component in the mixture. The upper limit on T'_b/T_b is established by the ethylene—n-heptane system. For systems containing an acetylene, a naphthene, or an aromatic as a component it is necessary to apply a correction factor to the boiling parameter. For these systems the behavior of the critical pressure ratio does not vary with the difference in boiling point properties of the components in the same manner as it does for paraffin and olefin systems. Figure 2 relates the corrected value of the boiling parameter to the calculated value for naphthenic and aromatic systems. Figure 3 gives the ratio of the corrected parameter to the calculated parameter for acetylene systems.

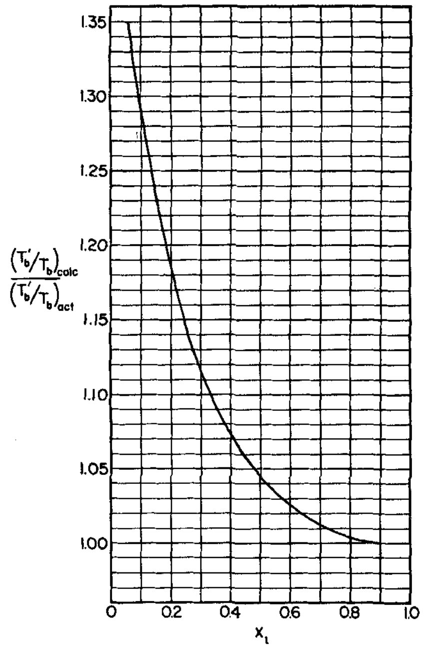

Fig. 3. Ratio of corrected boiling parameter to actual boiling parameter vs. x_l, mole fraction of low-boiling component for acetylene systems.

For the twenty nonmethane binary systems available the average deviation of the 105 compositions is 1.17%. This includes ten normal and isoparaffin systems (forty-eight compositions, 1.03%), four olefin-containing systems (twenty-three compositions, 1.54%), and six acetylene, naphthene, and aromatic systems (thirty-four compositions, 1.11%). The systems considered and the average deviation for each system are included as part of Table 1.

Multicomponent Systems

Figure 1 may also be used for the calculation of the critical pressures of nonmethane, multicomponent mixtures containing all types of hydrocarbons. For a ternary system the binary, consisting of the two high-boiling components, is considered first. The critical pressure of the binary is calculated, with the relative (low-boiling-free basis) mole fractions of the two components to establish the binary composition; then, P'_c, T_b, T'_b are calculated

TABLE 1. SYSTEMS INVESTIGATED AND CRITICAL PRESSURE DEVIATIONS

Binary systems	Number of mixtures	Average deviation, %
Ethane—propane (*24*)	6	1.42
Ethane—*n*-butane (*18*)	5	1.00
Ethane—*n*-pentane (*34*)	9	1.21
Ethane—*n*-heptane (*17*)	5	1.54
Propane—*n*-butane (*28*)	5	1.17
Propane—*n*-pentane (*37*)	4	1.16
Propane—isopentane (*40*)	5	1.58
n-butane—*n*-pentane (*11*)	1	1.16
n-butane—*n*-heptane (*19*)	5	0.61
n-pentane—*n*-heptane (*6*)	3	1.17
Ethane—propylene (*27*)	7	1.62
n-butane—ethylene (*42*)	1	1.72
n-heptane—ethylene (*20*)	8	0.82
Ethylene—propylene (*16*)	7	2.64
Ethane—cyclohexane (*21*)	8	1.13
Ethane—benzene (*22*)	6	0.58
Propane—benzene (*12*)	3	2.54
n-hexane—toluene (*41*)	3	3.25
Propane—acetylene (*26*)	8	0.69
Propylene—acetylene (*26*)	6	0.34
Multicomponent systems		
Ethane—propane—*n*-pentane (*11*)	1	1.48
Propane—*n*-butane—*n*-pentane (*11*)	1	2.14
n-butane—*n*-pentane—*n*-hexane (*11*)	1	1.25
Ethane—propane—*n*-butane—*n*-pentane (*11*)	1	1.89
Propane—*n*-butane—*n*-pentane—*n*-hexane (*11*)	1	0.46
Ethane—propane—*n*-butane—*n*-pentane—*n*-hexane (*11*)	1	1.10
Binary systems	Number of mixtures	Average deviation, %
Methane—ethane (*4*)	7	0.42
Methane—propane (*32*)	7	1.23
Methane—*n*-butane (*36*)	5	5.17
Methane—isobutane (*29*)	3	0.75
Methane—*n*-pentane (*38*)	5	0.97
Methane—isopentane (*1*)	2	1.95
Methane—*n*-heptane (*33*)	5	1.13
Multicomponent systems		
Methane—ethane—*n*-butane (*5*)	4	2.31
Methane—ethane—*n*-pentane (*3*)	2	1.85
Methane—propane—*n*-butane (*35*)	4	2.57
Methane—propane—*n*-pentane (*8*)	2	1.63
Methane—ethylene—isobutane (*2*)	2	1.02
Methane—ethane—propane—*n*-butane (*23*)*	1	3.07
Methane—ethane—propane—*n*-butane—*n*-pentane (*10*)	1	3.16
Methane—ethane—propane—*n*-pentane—*n*-hexane (*15*)	1	0.80
Methane—ethane—propane—*n*-butane—*n*-pentane—*n*-hexane (*11*)	1	0.63
Methane—ethane—propane—*n*-butane—*n*-pentane—*n*-hexane—*n*-heptane (*23*)*	1	3.04

$$\text{Average deviation, \%} = \frac{\text{calculated value} - \text{reported value}}{\text{reported value}} \times 100$$

* Mixture also contains small amounts of nitrogen and/or carbon dioxide.

and the critical pressure of the binary is determined from Figure 1. Next the ternary is considered, and T_b and T'_b are calculated in the manner described above for a multicomponent system. P'_c is calculated as the molar average of the critical pressure of the heavy binary. The critical pressure of the ternary is then established from Figure 1. For a four-component system the heaviest binary is again considered first, then the heaviest ternary, and finally the quaternary, determining the critical pressure of the binary for P'_c of the ternary and P_c of the ternary for P'_c of the quaternary. This procedure may be extended to any number of components. The necessity of a step-by-step method is obvious from Figure 1, since when the mole fraction of the low-boiling component becomes zero, P_c/P'_c becomes unity regardless of T'_b/T_b, and P'_c must be the actual critical pressure of the mixture of the remaining high-boiling components.

This procedure has been tested on six multicomponent mixtures with an average deviation of 1.36%. The results are included as part of Table 1.

TABLE 2. SYSTEMS INVESTIGATED AND CRITICAL DENSITY DEVIATIONS

Binary systems	Number of mixtures	Average deviation, %
Ethane—*n*-butane (*18*)	5	2.02
Ethane—*n*-pentane (*34*)	5	2.47
Ethane—*n*-heptane (*17*)	5	1.29
Propane—isopentane (*40*)	5	1.40
n-butane—*n*-heptane (*19*)	5	1.50
Ethane—propylene (*27*)	10	1.30
n-heptane—ethylene (*20*)	8	0.66
Ethane—cyclohexane (*21*)	5	1.56
Ethane—benzene (*22*)	6	2.37
n-hexane—toluene (*41*)	3	1.08
Methane—propane (*32*)	5	2.74
Methane—*n*-butane (*36*)	5	8.30
Methane—isobutane (*29*)	3	3.57
Methane—*n*-pentane (*38*)	5	1.07
Methane—*n*-heptane (*1*)	5	1.31

EXAMPLE CALCULATION 1

Determine the critical pressure of a hydrocarbon mixture having the following composition:

	Mole fraction	T_{bi}, °R.	P_{ci}, lb./sq. in. abs.
Ethane	0.254	331.7	707.1
Propane	0.255	416.1	617.4
n-butane	0.255	491.6	550.1
n-pentane	0.236	556.6	494.2

Establish the critical pressure on the n-butane—n-pentane binary

Binary composition:

$$n\text{-butane:}\quad \frac{0.255}{0.255 + 0.236} = 0.519$$

$$n\text{-pentane:}\quad \frac{0.236}{0.255 + 0.236} = 0.481$$

$$T'_b = 491.6\ (0.519) + 556.6\ (0.481) = 522.8\,^{\circ}\text{R.}$$

T_b [from Equation (1) and vapor pressure data] = 513.0°R.

$P'_c = 550.1\ (0.519) +$
$494.2\ (0.481) = 523.2$ lb./sq.in.abs.

From Figure 1 at $T'_b/T_b = 1.020$ and $x_l = 0.519$, $P_c/P_c' = 1.035$; $P_c = 541.5$ lb./sq. in. abs.

Establish the critical pressure of the propane—n-butane—n-pentane ternary

Ternary composition:

$$\text{propane} = \frac{0.255}{0.255+0.255+0.236} = 0.342$$

Similarly *n*-butane = 0.342 and *n*-pentane = 0.316

$T_b' = 416.1\ (0.342) + 491.6\ (0.342) + 556.6\ (0.316) = 486.3$°R.

T_b [from Equation (2) and vapor pressure data] = 455.0°R.

$P_c' = 617.4\ (0.342) + 541.5\ (0.342 + 0.316) = 567.4$ lb./sq. in. abs.

From Figure 1 at $T_b'/T_b = 1.069$ and $x_l = 0.342$, $P_c/P_c' = 1.095$; $P_c = 621.3$ lb./sq. in. abs.

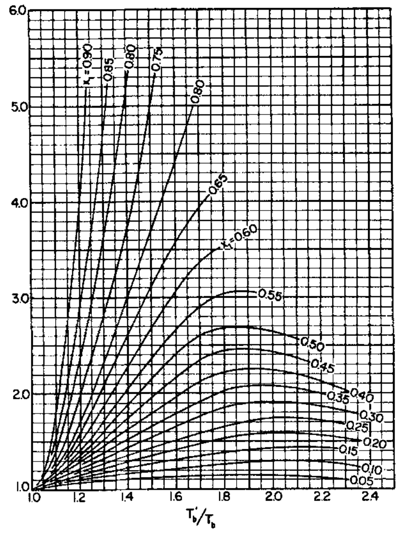

Fig. 4. Relationships between ρ_c/ρ'_c and T'_b/T_b for hydrocarbon systems containing methane.

Establish the critical pressure of the required quaternary

$T_b' = 331.7\ (0.254) + 416.1\ (0.255) + 491.6\ (0.255) + 556.6\ (0.236) = 446.5$°R.

T_b [from Equation (2) and vapor pressure data] = 381.0°R.

$P_c' = 707.1\ (0.254) + 621.3\ (0.255 + 0.255 + 0.236) = 642.9$ lb./sq. in. abs.

From Figure 1 at $T'_b/T_b = 1.172$ and $x_l = 0.254$, $P_c/P'_c = 1.176$; $P_c = 756.1$ lb./sq. in. abs.

Etter and Kay (*11*) report a value of 742 lb./sq. in. abs. for this mixture.

METHANE SYSTEMS

Binary Systems

Owing to the behavior of methane-containing systems, which differs from that of systems containing the other normal paraffins, a separate relationship was developed and appears as Figure 4. For binary systems, this figure is used in exactly the same manner as Figure 1 for nonmethane binary systems, where the mole fraction of low-boiling component is always the mole fraction of methane. The upper limiting value of T'_b/T_b corresponds to the methane—*n*-heptane system. For seven systems evaluated at thirty-four compositions the average deviation of calculated values from reported values is 1.58%. When one excludes the methane—*n*-butane system, which yields a disproportionately high error, the average deviation is 0.96%. The systems studied, together with the average deviations, are included as part of Table 1.

Multicomponent Systems

For mixtures containing more than two components the procedure is the same as for nonmethane systems, except for the final step in the calculation. Figure 1 is used to calculate the critical pressure of the heaviest binary, ternary, etc., which may include acetylenes, naphthenes, and aromatics; then, for the calculation of the critical pressure of the entire mixture, Figure 4 is used.

For multicomponent mixtures containing methane and ethane the critical pressure ratio tends to be higher than would normally be expected from the behavior of mixtures containing methane and other heavier boiling components. In such mixtures ethane appears to influence the critical pressure in a manner very similar to methane and quite unlike that of the higher boiling paraffins. For such systems it is recommended that the pure component boiling points of methane and ethane be corrected to 210° and 350°R. respectively. Again the calculation procedure is the same, except for the final step, in which T'_b of the total mixture is calculated with the corrected boiling points. For methane-ethane multicomponent mixtures this is the only correction necessary.

The critical pressures of complex mixtures containing up to 5 mole % of nitrogen and/or carbon dioxide may also be determined with the additional correction of the inclusion of the mole fractions of nitrogen and carbon dioxide with the methane content, yielding a corrected mole fraction of low-boiling component.

This method has been tested on five ternary methane systems, giving an average deviation of 1.58% for fourteen compositions. For five compositions from four, five, six, and seven component mixtures the average deviation is 2.14%. These results are also listed in Table 1.

EXAMPLE CALCULATION 2

Determine the critical pressure of a hydrocarbon mixture having the following composition:

	Mole fraction	T_{bi}, °R.	P_{ci}, lb./sq. in. abs.
Methane	0.461	200.7	673.1
Ethane	0.443	331.7	707.1
n-pentane	0.096	556.6	494.2

Establish the critical pressure of the ethane—n-pentane binary

Binary composition:

$$\text{ethane: } \frac{0.443}{0.443 + 0.096} = 0.822;$$

n-pentane = 0.178

$T'_b = 371.8$°R., $T_b = 338.0$°R., and $P'_c = 668.7$ lb./sq. in. abs.

From Figure 1 at $T'_b/T_b = 1.101$ and $x_l = 0.822$, $P_c/P'_c = 1.450$; $P_c = 969.6$ lb./sq. in. abs.

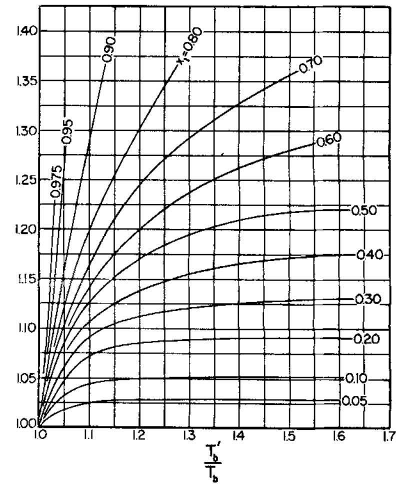

Fig. 5. Relationship between P_c/P'_c and T'_b/T_b for nonmethane hydrocarbon systems.

Establish the critical pressure of the required ternary

$T'_b = 210.0\ (0.461) + 350.0\ (0.443) + 556.6\ (0.096) = 305.4$°R.

(Note that in this step the corrected values of T_{b_i} are used for methane and ethane.)

T_b [from Equation (2) and vapor pressure data] = 218.0°R.

$P'_c = 673.1\ (0.461) + 969.6\ (0.443 + 0.096) = 833.9$ lb./sq. in. abs.

From Figure 4 at $T'_b/T_b = 1.400$ and $x_l = 0.461$, $P_c/P'_c = 1.780$; $P_c = 1{,}484$ lb./sq. in. abs.

Billman, Sage, and Lacey (*3*) report a value of 1,500 lb./sq. in. abs. for this mixture.

A rather accurate method has been developed for the prediction of the critical pressure of multicomponent hydrocarbon mixtures of known composition. These mixtures may contain normal and isoparaffins, olefins, acetylenes, naphthenes, and aromatics as components. Their critical pressures may be calculated from a knowledge of the pure component critical properties and vapor pressure behavior. For binary systems the expected error is approximately

1% and for multicomponent mixtures approximately 2%.

CRITICAL DENSITY

From an analysis of existing data for the molar density at the critical point of binary mixtures the behavior of the critical density ratio ρ_c/ρ'_c, where ρ'_c is the reciprocal of the molar average of the critical molar volumes of the pure components, is quite similar to that of the critical pressure ratio. There is a corresponding shift in maximum values and increase with greater differences in the properties of the pure components. The boiling parameter T'_b/T_b again may represent the differences in properties of the pure components.

NONMETHANE SYSTEMS

Based upon data for ten nonmethane binary systems the relationship between the critical density ratio ρ_c/ρ'_c and the boiling parameter T'_b/T_b is presented as Figure 5. The parameters are the mole fraction of low-boiling component in the mixture. The upper limit on T'_b/T_b is established by the ethylene—*n*-heptane system. For systems containing a naphthene or an aromatic as a component a correction is again needed. To calculate ρ'_c for a binary containing a naphthene the critical molar volume of the pure naphthene should be 0.960 times the actual value. For the calculation of ρ'_c for an aromatic containing binary the critical molar volume of the pure aromatic should be 0.935 times the actual value. For example the corrected critical molar volume of cyclohexane is equal to 0.960 (308) = 295 cc./g. mole.

For the ten available nonmethane containing binary systems and fifty-seven compositions the average deviation of calculated values from reported values is 1.53%. This includes five normal and isoparaffin systems (twenty-five compositions, 1.73%), two olefin containing systems (eighteen compositions, 1.01%), and three naphthene and aromatic systems (fourteen compositions, 1.83%). The systems considered and the average deviation for each system are included as part of Table 2.

EXAMPLE CALCULATION 3

Determine the critical density of a hydrocarbon mixture having the following composition:

	Mole fraction	T_{bi}, °R.	v_{ci}, cc./g.-mole
n-butane	0.631	491.6	255.0
n-heptane	0.369	669.0	426.4

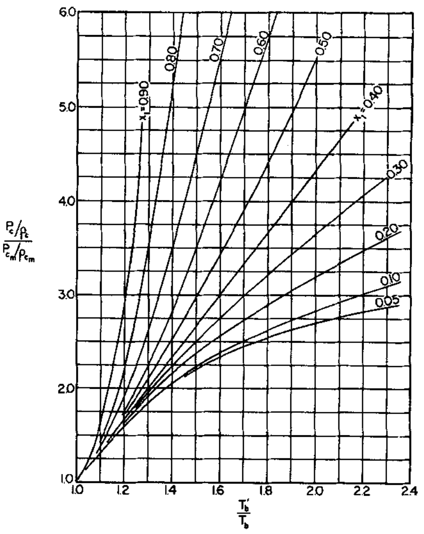

Fig. 6. Relationships between $\dfrac{P_c}{\rho_c} \Big/ \dfrac{P_{cm}}{\rho_{cm}}$ and $\dfrac{T'_b}{T_b}$ for methane systems.

$T'_b = 491.6\ (0.631) + 669.0\ (0.369) = 557.0$°R.; $T_b = 513.9$°R.

$\rho'_c = 1/v'_c = 1/[255.0\ (0.631) + 426.4\ (0.369)] = 0.00314$ g.-moles/cc.

From Figure 5 at $T'_b/T_b = 1.085$ and $x_1 = 0.631$, $\rho_c/\rho'_c = 1.133$, $\rho_c = 1.133\ (0.00314) = 0.00356$ g.-moles/cc.

Kay (*19*) reports a value of 0.00353 g.-moles/cc. for this mixture.

METHANE SYSTEMS

For the five methane containing systems for which critical density data were available more internal consistency was apparent when the ratio P_c/ρ_c was correlated instead of ρ_c alone.

The relationship between $\dfrac{P_c}{\rho_c} \Big/ \dfrac{P_{cm}}{\rho_{cm}}$, where P_{cm} and ρ_{cm} are the critical pressure and critical molar density of pure methane, and T'_b/T_b is presented as Figure 6. The parameters are the mole fraction of the low-boiling component in the mixture, and the limit on T'_b/T_b corresponds to the methane—*n*-heptane system. It is important to note that this relationship is based on the calculated values of the critical pressures of methane containing systems rather than the reported experimental values. By using this approach the error in the critical pressure estimate is not included when the critical density is calculated.

The average deviation of calculated values from reported values of five systems evaluated at twenty-three compositions is 1.58%. The systems studied, together with the average deviations, are included as part of Table 2.

EXAMPLE CALCULATION 4

Determine the critical density of a hydrocarbon mixture of the following composition:

	Mole fraction	T_{bi}, °R.	P_{ci}, lb./sq. in. abs.	v_{ci}, cc./g.-mole
Methane	0.529	200.7	673.1	99.0
n-pentane	0.471	556.6	494.2	311.0

Calculate the critical pressure of the mixture

$T'_b = 368.5$°R., $T_b = 215.4$°R., $P'_c = 588.1$ lb./sq. in. abs.

From Figure 4 at $T'_b/T_b = 1.710$ and $x_1 = 0.529$, $P_c/P'_c = 2.79$; $P_c = 1640$ lb./sq. in. abs.

Calculate the critical density of the mixture

From Figure 6 at $T'_b/T_b = 1.710$ and x_1

$$= 0.529, \frac{P_c}{\rho_c} \Big/ \frac{P_{cm}}{\rho_{cm}} = 4.27$$

$$\rho_c = 1{,}640 \left(\frac{1}{99.0}\right) \Big/ 4.27\ (673.1)$$

$$= 0.00577 \text{ g.-moles/cc.}$$

Sage, Reamer, Olds, and Lacey (*38*) report a value of 0.00576 g.-moles/cc. for this mixture.

No data appear to be reported in the literature for the critical densities of multicomponent mixtures. However from the analogy to critical pressure behavior it is felt that Figure 5 may be used to estimate the critical density of multicomponent mixtures not containing methane, with the step-by-step calculation procedure described for the critical pressure.

A rather accurate method is presented for the prediction of the critical density of binary hydrocarbon mixtures containing normal and isoparaffins, olefins, naphthenes, and aromatics. The expected error is approximately 2%. It is anticipated that this correlation may be extended to multicomponent mixtures.

NOTATION

P_c = critical pressure of mixture, lb./sq. in. abs.

P'_c = pseudocritical pressure of mixture (method of calculation depends on number of components), lb./sq. in. abs.

P_{ci} = critical pressure of pure *i*th component, lb./sq. in. abs.

P_{cm} = critical pressure of pure methane, lb./sq. in. abs.

P_i = vapor pressure of *i*th component, lb./sq. in. abs.

T_b = atmospheric boiling point of mixture, °R.

T'_b = molar-average boiling point of mixture, °R.

T_{bi} = normal boiling point of pure *i*th component, °R.

v'_c = pseudocritical molar volume of mixture, cc./g.-mole

v_{ci} = critical molar volume of pure *i*th component, cc./g.-mole

x_i = mole fraction of *i*th component
x_l = mole fraction of low-boiling component
π = total pressure, lb./sq. in. abs.
ρ_c = critical molar density of mixture, g.-moles/cc.
ρ'_c = pseudocritical molar density of mixture, g.-moles/cc.
ρ_{cm} = critical molar density of pure methane, g.-moles/cc.

LITERATURE CITED

1. Amick, E. H., W. B. Johnson, and B. F. Dodge, *Chem. Eng. Progr. Symposium Ser. No. 3*, **48**, 65 (1952).
2. Benedict, Manson, Ernest Solomon, and L. C. Rubin, *Ind. Eng. Chem.*, **37**, 55 (1945).
3. Billman, G. W., B. H. Sage, and W. N. Lacey, *Trans. Am. Inst. Mining Met. Engrs.*, **114**, 13 (1948).
4. Bloomer, O. T., D. C. Gami, and J. D. Parent, *Inst. Gas Technol. Research Bull. No.* 22 (July, 1953).
5. Cota, H. M., M.S. thesis, Northwestern Univ., Evanston, Illinois (1960).
6. Cummings, L. W. T., F. W. Stone, and M. A. Volante, *Ind. Eng. Chem.*, **25**, 728 (1933).
7. Davis, P. C., A. F. Bertuzzi, T. L. Gore, and Fred Kurata, *J. Petrol. Technol.*, **6**, 37 (1954).
8. Dourson, R. H., B. H. Sage, and W. N. Lacey, *Trans. Am. Inst. Mining Met. Engrs.*, **151**, 206 (1943).
9. Eilerts, C. K., et al., "Phase Relations of Gas-Condensate Fluids," Vol. 1, pp. 101-154, Monograph No. 10, U.S. Bureau of Mines (1957).
10. Etter, D. O., Ph.D. thesis, Ohio State Univ., Columbus, Ohio (1960).
11. Etter, D. O., and W. B. Kay, *J. Chem. Eng. Data*, **6**, 409 (1961).
12. Glanville, J. W., B. H. Sage, and W. N. Lacey, *Ind. Eng. Chem.*, **42**, 508 (1950).
13. Grieves, R. B., and George Thodos, *A.I.Ch.E. Journal*, **6**, 561 (1960).
14. *Ibid.*, **8**, 550 (1962).
15. Hanson, G. H., and G. G. Brown, *Ind. Eng. Chem.*, **37**, 821 (1945).
16. Haselden, G. G., F. A. Holland, M. B. King, and R. F. Strickland-Constable, *Proc. Roy. Soc. (London)*, **240A**, 1 (1957).
17. Kay, W. B., *Ind. Eng. Chem.*, **30**, 459 (1938).
18. *Ibid.*, **32**, 353 (1940).
19. *Ibid.*, **33**, 590 (1941).
20. *Ibid.*, **40**, 1459 (1948).
21. *Ibid.*, **48**, 422 (1956).
22. ———, and T. D. Nevens, *Chem. Eng. Progr. Symposium Ser. No. 3*, **48**, 108 (1952).
23. Kurata, Fred, and D. L. Katz, *Trans. Am. Inst. Chem. Engrs.*, **38**, 995 (1942).
24. Matschke, D. E., and George Thodos, *J. Chem. Eng. Data*, **7**, 232 (1962).
25. Mayfield, F. D., *Ind. Eng. Chem.*, **34**, 843 (1942).
26. McCurdy, J. L., and D. L. Katz, *Oil Gas J.*, **43**, 102 (1945).
27. McKay, R. A., H. H. Reamer, B. H. Sage, and W. N. Lacey, *Ind. Eng. Chem.*, **43**, 2112 (1951).
28. Nysewander, C. N., B. H. Sage, and W. N. Lacey, *ibid.*, **32**, 118 (1940).
29. Olds, R. H., B. H. Sage, and W. N. Lacey, *ibid.*, **34**, 1008 (1942).
30. Organick, E. I., *Chem. Eng. Progr., Symposium Ser. No. 6*, **49**, 81 (1953).
31. ———, and G. G. Brown, *Chem. Eng. Progr. Symposium Ser. No. 2*, **48**, 97 (1952).
32. Reamer, H. H., B. H. Sage, and W. N. Lacey, *Ind. Eng. Chem.*, **42**, 534 (1950).
33. *Ibid., Data Series*, No. 1, 29 (1956).
34. Reamer, H. H., B. H. Sage, and W. N. Lacey, *J. Chem. Eng. Data*, **4**, 44 (1959).
35. Rigas, T. J., D. F. Mason, and George Thodos, *ibid.*, p. 201.
36. Sage, B. H., B. L. Hicks, and W. N. Lacey, *Ind. Eng. Chem.*, **32**, 1085 (1940).
37. Sage, B. H., and W. N. Lacey, *ibid.*, p. 992.
38. Sage, B. H., H. H. Reamer, R. H. Olds, and W. N. Lacey, *ibid.*, **34**, 1108 (1942).
39. Smith, R. L., and K. M. Watson, *ibid.*, **29**, 1408 (1937).
40. Vaughn, W. E., and F. C. Collins, *ibid.*, **34**, 885 (1942).
41. Watson, L. M., and B. F. Dodge, *Chem. Eng. Progr., Symposium Ser. No. 3*, **48**, 73 (1952).
42. Williams, Brymer, Ph.D. thesis, Univ. Michigan, Ann Arbor, Michigan (1947).

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Interrelation of Packing and Mixed Phase Flow Parameters with Liquid Residence Time Distribution

M. B. GLASER and IRA LICHTENSTEIN
Esso Research and Engineering Company, Linden, New Jersey

Brine-air and kerosene-hydrogen systems were used for the mixed phase tests. No specific gas phase effects were detected. The measured variability, encompassing all three flow mechanisms, correlated well with particle Reynolds number for each system and decreased with increasing flow rate. However the variability component resulting solely from bulk liquid flow through the main bed channels was found to be relatively constant over a wide range of Reynolds number and independent of whether the bed was uniformly packed or contained large packing faults. The significance of these results to liquid-solids contacting efficiency is discussed .

The majority of previous publications which considered flow characteristics of packed beds have dealt with single-phase gas or liquid flow. In addition the bulk of these publications were based on theoretical models which used one of three approaches: piston flow, eddy diffusion, or void cell mixing (*1, 2, 3, 5, 6, 8*).

The use of tracer techniques is becoming increasingly popular for obtaining fluid dispersion and residence time distribution data in packed bed flow via transient response methods. The procedure generally involves the predetermined addition of a tracer stream to the entering liquid and time

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Ira Lichtenstein is with The Lummus Company, New York, New York.