V_c = critical volume, cm^3/g
V_r = reduced volume, V/V_c
Z_c = critical compressibility factor
Z_{RA} = constant of modified Rackett equation
β_s = liquid compressibility at saturation
ρ = liquid density, g/cm^3
ρ_c = critical density, g/cm^3
ρ_r = reduced density, ρ/ρ_c
ρ_s = saturated liquid density, g/cm^3
ρ_{rs} = reduced saturation liquid density, ρ_s/ρ_c
ω = acentric factor

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Prediction of Bubble-Point Density of Mixtures

Calvin F. Spencer and Ronald P. Danner[1]
Department of Chemical Engineering, The Pennsylvania State University, University Park, Pa. 16802

Methods for predicting the density of mixtures at their bubble points have been extensively evaluated. Two analytical methods for pure compounds recently reported by the authors—the modified Rackett equation and the generalized polynomials representing the Lu chart—have been extended to mixtures. On the basis of a comparison of the experimental densities of a series of binary systems with those predicted by these methods and the equations of others, a modification of the Rackett equation is recommended for its accuracy and versatility. For mixtures containing only hydrocarbons, the average percent error in the predicted bubble-point densities was less than 2. The method of Harmens was essentially equivalent in accuracy for the systems studied. Results for systems containing a nonhydrocarbon suggest that larger errors should be expected for such systems.

The authors have recently reported that a modified version of the Rackett equation and an analytical form of the Lu chart are accurate methods of predicting the liquid density of pure compounds (*22*, *31*). To be of real practical value, these methods must be shown to be applicable to mixtures.

Available Correlations

A number of investigators have developed equations for predicting the bubble-point density of mixtures. Ritter et al. (*27*) have presented a nomograph for calculating the specific gravity of paraffinic hydrocarbon mixtures at their bubble points. This procedure requires only the average molecular weight of the mixture, but is limited to molecular weights less than 100. It has the disadvantage of being available only in a graphical form, and thus is not readily applied to a large number of data points or in a computer program.

Harmens (*5*, *6*) has developed a correlation in the following form:

$$\frac{1}{V_{bp}} = \rho_{bp} = C \cdot F(T_r) \qquad (1)$$

C is a constant which has been specified for a number of compounds in the range of C_1 to C_7. When no specific C value is available, a value can be predicted by Equation 2.

$$C = \rho_c\,[0.43875 - 0.625\,Z_c] \qquad (2)$$

$F(T_r)$ was originally given in tabular form. In the present evaluation, a regression analysis was used to transform this tabular function into the following analytical form:

$$F(T_r) = 15.81 - 17.71\,T_r + 22.67\,T_r^2 + 15.07\,T_r^3 \qquad (3)$$

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[1] To whom correspondence should be addressed.

This third-order polynomial reproduced the tabulated values of $F(T_r)$ with an average percent error of 0.36 and a maximum percent error of 1.7. To compute the average C value for a mixture, Harmens recommended use of the reciprocal of the weight average of $1/C$. The reduced temperature for use in this correlation is based on an average critical temperature defined as

$$T_{c(\mathrm{av})} = \sum_{i=1}^{n} r_i T_{ci} \tag{4}$$

where r_i is the arithmetic average of the mole fraction and mass fraction of the ith component.

A method suggested by Phillips and Thodos (*20*) is based on the law of rectilinear diameters and the equation of Guggenheim (*3*). The final equation for the bubble-point density of mixtures is

$$\rho r_{bp} = \tfrac{1}{2}[3.05\, m^{15/8} - 1.5\, m^{5/2}\, T_r]^{1/m} + 5.45\, n\, [1 - T_r]^{n} \tag{5}$$

The constants m and n in this equation have been presented graphically in terms of the atmospheric bubble-point temperature, the atmospheric dewpoint temperature, and the molar average value of the normal boiling point of the component. In the determination of both the bubble-point and the dew-point temperatures, trial and error procedures are required in which some estimate of the vapor–liquid equilibrium constants must be incorporated. Thus, this procedure becomes rather tedious in practice.

Rackett has suggested the following equation in a paper extending his equation for the saturated liquid density of pure compounds to the bubble-point density of hydrocarbon mixtures (*21*):

$$\left[\frac{1}{\rho_{bp}}\right] = V_{bp} = V_{cm} Z_{cm}^{\left[1 - \frac{T}{T_{cb}}\right]^{2/7}} \tag{6}$$

where V_{cm} and Z_{cm} are molar averages of the pure component critical volumes and critical compressibility factors. T_{cb}, which is essentially a pseudocritical temperature, is given by Equation 7:

$$T_{cb} = \sum_{i=1}^{n} x_i b_i T_{ci} \Big/ \sum_{i=1}^{n} x_i b_i \tag{7}$$

where the b_i's are weighting factors and are given by

$$b_i = \exp\left[(6.33 \times 10^{-4}) \cdot \sum_{j=1}^{n} x_i\, (T_{ci} - T_{cj})^{9/7} + \ln C_i\right] \tag{8}$$

The C_i in this equation is a weighting factor adjustment which is zero for aliphatic hydrocarbons and for which a specific value has been determined for some aromatic hydrocarbons, nonhydrocarbons, and naphthenes (*21*).

Extension of Rackett Equation to Mixtures

The authors have recently reported an extensive evaluation of a form of the Rackett equation for predicting the saturated liquid density of pure compounds (*31*).

$$\frac{1}{\rho_s} = \left[\frac{RT_c}{P_c}\right] Z_{RA}^{[1 + (1 - T_r)^{2/7}]} \tag{9}$$

In this equation the Z_{RA} is a specified constant which has been tabulated for many materials. (If no Z_{RA} is available, Z_c can be used as a reasonable approximation.) Equation 9 has now been extended to mixtures. On the basis of a careful analysis of the numerous possible methods of arriving at optimum combining rules for the critical constants of the mixtures, the following equations are recommended.

$$\left[\frac{1}{\rho_{bp}}\right] = V_{bp} = R\left[\sum_{i=1}^{n} x_i \frac{T_{ci}}{P_{ci}}\right] Z_{RAm}^{[1 + (1 - T_r)^{2/7}]} \tag{10}$$

$$Z_{RAm} = \sum_{i=1}^{n} x_i Z_{RAi} \tag{11}$$

A number of different pseudocritical temperature rules were also tested for calculating the reduced temperature required in the exponent of Equation 10. These included the molar average of the critical temperatures of the pure components (Kay's rule), Equations 7 and 8 as suggested by Rackett, the method of Li, and the equations of Chueh and Prausnitz. These latter two independent methods of predicting pseudocritical temperatures are defined below.

Li (*17*) suggested using a critical-volume average of the pure component critical temperatures.

$$T_{cm} = \sum_i \Phi_i T_{ci} \tag{12}$$

$$\Phi_i = \frac{x_i V_{ci}}{\sum_i x_i V_{ci}} \tag{13}$$

Chueh and Prausnitz (*2*) suggested a more complicated definition also making use of the critical-volume fraction.

$$T_{cm} = \sum_i \sum_j \Phi_i \Phi_j T_{cij} \tag{14}$$

$$T_{cij} = \sqrt{T_{ci} T_{cj}}\,(1 - k_{ij}) \tag{15}$$

$$k_{ij} = 1.0 - \left[\frac{\sqrt{V_{ci}^{1/3} V_{cj}^{1/3}}}{[V_{ci}^{1/3} + V_{cj}^{1/3}]/2}\right]^3 \tag{16}$$

In Figure 1 the critical-temperature loci predicted by the above methods are shown for the ethene-n-heptane system together with the experimental data of Kay (*10*). The results shown are typical of those for a number of systems tested. The Li equation most closely predicts the true critical temperatures; the rule of Kay gives the lowest predicted values; and the methods of Chueh-Prausnitz and Rackett fall close to one another somewhere in between. In many correlations, however, the best pseudocritical rule is not the one which most accurately predicts the true critical values. On the other hand, a problem arises for a data point which falls in the region between the true critical locus and the locus predicted by a particular pseudocritical method. In this case a reduced temperature greater than one is obtained, a circumstance which most of the correlations cannot handle analytically. Thus, the number of applicable data points varied with the pseudocritical temperature rule. As would be expected from Figure 1, the method of Li accepted the largest number of points and that of Kay the least.

Analytical Form of Lu Chart

The chart of Lu (*18*) for predicting the effect of pressure on liquid densities can also be used to predict bubble-point densities of mixtures. This laboratory has recently reported a set of generalized polynomials for calculating the density-correlation factor of the Lu chart as a function of reduced temperature and reduced pressure

(22). Using this density correlation factor, K, the bubble-point density can be obtained as follows:

$$\rho_{bp} = \frac{K_{bp}}{K_R} \rho_R \qquad (17)$$

where subscript R refers to some reference density for the composition of interest.

To obtain the reduced pressure required for the generalized polynomials, the molar average of the critical pressures of the components was used. The reduced temperature was calculated using a molar average of the critical temperatures or the pseudocritical temperature rules of Chueh-Prausnitz (2) and Li (*17*). The reference density was calculated in general using a molar average of the pure component densities at 60°F and 1 atm as obtained from "Tech. Data Book—Petrol. Refining" (*1*). For ethane- and ethene-containing mixtures, the reference densities were calculated at −30°F and the corresponding vapor pressure of these compounds. For mixtures containing propane or propene, the temperature was 60°F, but the pressure used was the corresponding pure component vapor pressure at 60°F. For methane in a mixture, a hypothetical density at 60°F and 1 atm was used (0.2995 g/cc). When the reference temperature and pressure selected for the low molecular weight component are not 60°F and 1 atm, the density of the heavier component must be corrected to the respective reference values.

Bubble-Point Density Data

The hydrocarbon mixture data used in this study consisted of almost 700 experimental data points for 19 different binary systems. (The references for the data are included in Table III.) Unfortunately, very few data were available for mixtures containing aromatics and naphthenes. The hydrocarbon-nonhydrocarbon data consist largely of values abstracted from the work of Kay and Sage and Lacey. These were the only data that could be found for nonhydrocarbon systems.

Results for Hydrocarbon Systems

The graphical method of Ritter et al. (27) required hand calculations and thus was evaluated with only a small portion of the data set. The data selected consisted of the ethane-*n*-butane, ethane-*n*-heptane, *n*-butane-*n*-heptane, and ethene-*n*-heptane systems. These same data were then used with Equation 10, using the Chueh-Prausnitz rule for pseudocritical temperature (Table I). Equation 10 gave considerably better results than the Ritter et al. chart. These same sets of data were considered in the paper by Phillips and Thodos (*20*), in which they quoted an average error of 4.8%. On the basis of the above, the methods of Ritter et al. and of Phillips and Thodos were eliminated from further consideration.

By use of the entire data set, Equation 10 and the generalized polynomials for the Lu chart were evaluated with a number of pseudocritical temperature rules. Throughout all the evaluations, points with a predicted reduced temperature greater than 0.97 were eliminated from the data set. In Table II a summary of these evaluations is given. The best result (1.76% average deviation) was obtained by the use of Equation 10 with the Chueh-Prausnitz pseudocritical temperature rule. The Lu chart polynomials also gave their best result (2.65% average deviation) with the Chueh-Prausnitz pseudocritical temperature rule.

In Table III a detailed comparison is given for the methods of Harmens and of Rackett and Equation 10 with the Chueh-Prausnitz pseudocritical temperature rule. The Rackett equation gives the largest deviation and bias. The method of Harmens and Equation 10 are es-

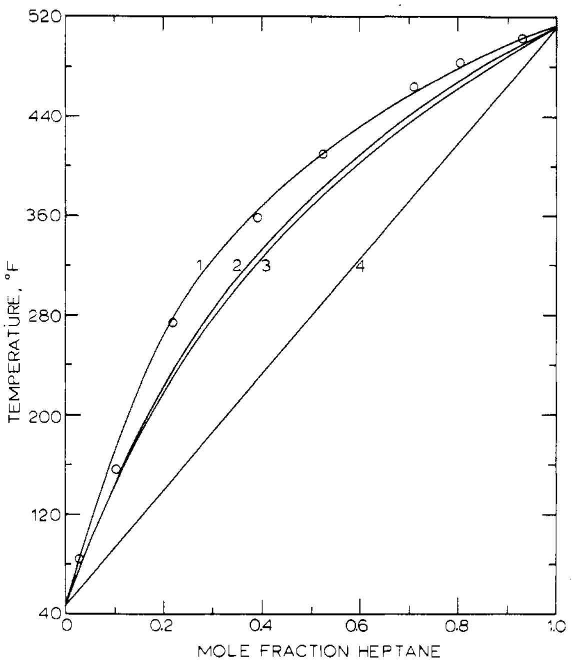

Figure 1. Comparison of pseudocritical temperature profiles for ethene-*n*-heptane system

0. Experimental data (*10*)
1. Li equation
2. Chueh-Prausnitz equation
3. Rackett equation
4. Kay's rule (molar average)

Table I. Comparison of Chart of Ritter et al. (*27*) and Equation 10

	Ritter et al. chart		Equation 10[a]	
Binary	Data points done	Av % error[b]	Data points done	Av % error[b]
Ethane-*n*-butane	44	4.29	38	0.94
Ethane-*n*-heptane	38	2.46	45	1.23
Butane-*n*-heptane	11	0.47	24	0.38
Ethene-*n*-heptane	30	4.14	33	1.33
Overall	123	3.35	140	1.03

[a] Chueh-Prausnitz rule for pseudocritical temperature. [b] Defined in Table II.

Table II. Evaluation of Equation 10 and Generalized Polynomials of Lu Chart

Method	Pseudocritical temp rule	Data points done	Av % error[a]	Bias[b]
Equation 10	Kay	584	5.76	−5.69
	Rackett	695	2.80	0.10
	Chueh and Prausnitz	692	1.76	−0.49
	Li	727	2.64	2.06
Lu chart polynomials	Kay	584	2.86	−2.02
	Chueh and Prausnitz	692	2.65	1.79
	Li	727	4.20	−3.62

[a] 100/N Σ|calculated value − experimental value/experimental value|.
[b] 100/N Σ(calculated value − experimental value)/experimental value.

sentially equivalent in accuracy, although Equation 10 has a larger bias. On the other hand, Equation 10 gave smaller average errors for 12 of the 19 systems.

Results for Systems Containing Nonhydrocarbons

The method of Harmens and Equation 10 were also evaluated for the prediction of the bubble-point densities in binary systems containing a hydrocarbon and an inorganic compound (except for the hydrogen sulfide-carbon dioxide system). The results for a representative set of data from the indicated references are given in Table IV. For the hydrogen-containing system, "classical" values for the critical temperature, critical pressure, and critical compressibility factor of hydrogen were used as recommended by Gunn et al. (*4*). The results are reasonable but poorer than those of the hydrocarbon systems, even though the data were restricted such that the mole fraction of carbon dioxide was always less than 0.5 and the mole fraction of hydrogen never more than 0.45. If these limitations were not adhered to, the errors frequently became excessive (30% or more).

For the systems of Table IV there is no apparent criterion for recommending Harmens' method or Equation 10. Equation 10 was better for six of the ten systems but considerably poorer for three of the other systems. For all the data points both methods give 2.9% average deviation. For most systems, both methods are so strongly biased either positively or negatively that the average deviation and bias are nearly equal.

Conclusions

For predicting the bubble-point densities of hydrocarbon mixtures, Equation 10, which is an extension of the Rackett equation, will give an accuracy equivalent to any

Table III. Comparison of Methods for Predicting Bubble-Point Density of Hydrocarbon Systems

		Harmens			Rackett			Equation 10		
System	Data Ref.	Data points done	Av % error	Bias	Data points done	Av % error	Bias	Data points done	Av % error	Bias
Methane-propane	(*29*)	4	1.58	−0.99	4	1.84	−1.84	4	0.51	−0.14
Methane-*n*-butane	(*29*)	20	4.18	−4.18	21	2.32	−2.32	21	3.02	−3.02
Methane-*n*-pentane	(*29*)	17	3.36	−3.36	19	2.32	2.03	19	3.18	−3.18
Methane-*n*-heptane	(*26*)	34	3.62	−3.62	36	2.33	−2.28	34	4.11	−4.11
Ethane-*n*-butane	(*8*)	37	0.45	0.21	36	1.60	−1.60	38	0.94	0.94
Ethane-*n*-heptane	(*7*)	43	1.46	0.57	44	1.67	−1.50	45	1.23	0.09
Ethane-*n*-decane	(*23*)	92	1.73	−0.48	98	2.28	2.19	99	2.20	−2.15
Ethane-cyclohexane	(*12*)	52	2.28	2.14	53	4.41	4.41	52	2.13	2.10
Ethane-propene	(*29*)	26	0.60	0.21	26	2.89	2.89	26	0.78	0.64
Ethane-benzene	(*15*)	51	3.24	1.72	53	9.48	9.30	51	2.89	2.48
Propane-*n*-butane	(*11*)	20	1.59	1.59	20	0.34	0.03	20	1.26	1.26
Propane-*n*-pentane	(*11*)	37	1.20	−0.89	38	1.40	−0.71	38	1.18	−1.16
Propane-*n*-decane	(*25*)	48	1.26	0.86	49	1.36	1.11	49	2.12	−1.73
Propane-benzene	(*28*)	44	1.93	0.65	45	3.60	3.51	42	0.97	0.93
Butane-*n*-heptane	(*9*)	24	0.74	0.62	24	1.39	−1.39	24	0.38	−0.32
Butane-*n*-decane	(*30*)	55	0.85	0.85	56	0.96	0.95	56	1.53	−1.41
Ethene-*n*-heptane	(*10*)	32	1.56	0.40	33	1.94	0.85	33	1.33	0.06
Propene-propane	(*28*)	8	0.42	0.39	8	0.78	−2.33	8	1.35	0.35
Propene-1-butene	(*28*)	32	0.46	0.41	32	0.91	−0.52	33	0.33	−0.19
Overall		676	1.72	0.13	695	2.63	1.45	692	1.76	−0.49

Table IV. Comparison of Method of Harmens and Equation 10 for Systems Containing Nonhydrocarbons

		Harmens			Equation 10[a]		
Binary mixture	Data Ref.	Data points done	Av % error	Bias	Data points done	Av % error	Bias
Methane-hydrogen sulfide	(*28*)	27	3.10	−2.90	23	0.96	−0.95
Ethane-hydrogen sulfide	(*14*)	22	7.45	−7.45	20	3.25	−3.25
Hydrogen-*n*-hexane	(*19*)	20	5.39	5.39	20	4.57	4.57
Hydrogen sulfide-propane	(*16*)	32	3.55	−3.09	32	2.51	−1.20
Hydrogen sulfide-pentane	(*28*)	25	2.34	−2.13	25	1.86	−1.10
Hydrogen sulfide-decane	(*28*)	23	0.78	−0.21	24	4.23	4.22
Carbon dioxide-propane	(*28*)	31	3.06	−2.97	33	5.82	−5.82
Carbon dioxide-butane	(*28*)	16	0.91	−0.85	17	3.84	−3.84
Carbon dioxide-decane	(*24*)	57	1.80	1.59	59	1.48	1.48
Hydrogen sulfide-carbon dioxide	(*13*)	20	1.94	−0.33	20	2.21	−1.11
Overall		273	2.92	−1.15	273	2.91	−0.56

[a] Chueh-Prausnitz rule for pseudocritical temperature.

available method. Previously the authors have shown that for predicting the saturated liquid density of pure compounds the Rackett equation is accurate, simple, and versatile (*31*). The extension of this correlation to mixtures should prove useful in numerous applications.

For the systems of Tables III and IV Harmen's method for predicting bubble-point densities is essentially equivalent in accuracy to Equation 10. In order to maintain this accuracy, however, both Harmen's method and the proposed method require one empirical constant (C for the method of Harmens and Z_{RA} for Equation 10). One contrast in the two methods is the range of compounds for which they can be applied. Whereas Harmens' method was developed mainly for hydrocarbons in the C_1–C_7 range, the modified Rackett equation has been shown to be reliable for heavier hydrocarbons, organic compounds, and inorganic compounds (*31*).

Nomenclature

K = correlating parameter of Lu chart
N = number of data points
P_c = critical pressure, atm
P_r = reduced pressure, P/P_c
R = universal gas constant, 82.06 atm cm^3/g mol K
T = temperature, K
T_c = critical temperature, K
T_{cm} = pseudocritical temperature of mixture, K
T_r = reduced temperature, T/T_{cm}
V_{bp} = bubble-point volume, cm^3/g mol
V_{cm} = pseudocritical volume of mixture, cm^3/g mol
V_s = volume of saturated liquid, cm^3/g mol
Z_c = critical compressibility factor
Z_{cm} = critical compressibility factor for mixture
Z_{RA} = constant of modified Rackett equation

Greek Letters

ρ_{bp} = bubble-point density, g mol/cm^3
ρ_c = critical density, g mol/cm^3
ρ_r = reduced density, ρ/ρ_c
ρ_s = saturated liquid density, g mol/cm^3

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Saturated Liquid Molar Volumes. The Rackett Equation

Tomoyoshi Yamada and Robert D. Gunn[1]
Chemical Engineering, University of Wyoming, Laramie, Wyo. 82070

A slightly modified form of the generalized Rackett equation is presented which improves its predictive accuracy by about an order of magnitude.

Rackett (*7*) recently proposed an unusually simple generalized equation for predicting liquid volumes. The accuracy of this equation, however, is only moderate. Spencer and Danner (*9*) found average deviations of 2.40% between calculated and experimental liquid volumes. These latter investigators have also modified this equation to predict liquid volumes with high accuracy, but the modified relationship is no longer entirely generalized because it requires one curve fitted constant for each pure compound. A generalized form of the Rackett equation is proposed here which is also very accurate.

$$V = V_{scr} Z_{cr}^{(1-T_R)^{2/7}} \tag{1}$$

where

$$Z_{cr} = 0.29056 - 0.08775\,\omega$$

and where V_{scr} is defined as

$$V_{scr} = V' \exp\left[-(1 - T'_R)^{2/7} \ln (0.29056 - 0.08775\,\omega)\right] \tag{2}$$

The original Rackett equation used the critical volume and the critical compressibility factor as parameters. Both are subject to large experimental errors which hamper seriously the predictive accuracy of the Rackett equation. The proposed relationship circumvents these problems.

One liquid density is required to calculate the scaling volume, V_{scr}, but this is not a shortcoming for a generalized relationship. For every compound for which critical volumes have been determined liquid molar volumes are

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[1] To whom correspondence should be addressed.