T = absolute temperature
x_i = mole fraction of component i in solution
γ_i = activity coefficient of component i in general
$\gamma_{i,j}$ = activity coefficient of component i in the $i - j$ binary
γ_i^F = factor defined by Equation (34) or (56)
γ_i^R = factor defined by Equation (23)

Superscripts

$*$ = unsymmetric normalization of activity coefficients
∞ = value at infinite dilution
$'$ = value for solute-free mixture

Subscripts

s = solvent species
σ = solute species

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A New Correlation for Saturated Densities of Liquids and Their Mixtures

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A new correlation has been developed for the densities of saturated liquids and their mixtures. The correlation is relatively easy to use and is applicable to a wide variety of liquids. The saturated liquid density correlation is flexible and consistent and requires only reduced temperature, acentric factor, and a characteristic volume for each pure compound. Mixing rules are given. When tested against a data base of 2 657 points of pure compound liquid density data for 97 hydrocarbons and 1 851 points for 103 other compounds, the new correlation gave an average absolute error of 0.37% compared to 2.14% for the Yen-Woods correlation and 0.50% for the SDR equation as modified by Spencer and Danner. For 2 994 points of liquid mixture density data for 167 mixtures, the new correlation gave an average absolute error of 1.40% compared to 5.64% for the Yen-Woods correlation and 2.95% for the SDR equation. Characteristic volumes are listed for 200 compounds; they are generalized as functions of acentric factor for various types of compounds and are compared to critical volumes.

SCOPE

The objective of this work was to develop and extensively test an equation for the computation of saturated liquid densities of pure compounds and their bubble point mixtures that has the following attributes: sufficiently general to apply to a wide range of compound classes, flexible enough to allow accurate calibration to known pure compound data, predictive in those cases where such data are unavailable or of uncertain accuracy, mathematically consistent in that there are no discontinuities in the value or slope in the range $0.25 < T_R < 0.98$, capable of being calibrated to mixtures for precise work, and simple enough for inclusion in process simulators and on microprocessors. In order to provide extensive testing and evaluation, it was necessary to develop an experimental data base representative of the wide variety of compounds and mixtures of interest.

CONCLUSIONS AND SIGNIFICANCE

A corresponding states equation which explicitly relates the saturated liquid volume of a pure compound to its reduced temperature and a readily available parameter, termed the characteristic volume, has been developed. The characteristic volumes are reported for 200 pure compounds. An evaluated set of mixing rules is presented.

The saturated liquid volumes obtained from the corresponding states liquid density (COSTALD) equation reproduce 4 508 points of experimental data on 190 different compounds to within 0.375 average absolute percent over the reduced temperature range of $0.25 < T_R < 0.98$. For 141 binary systems, 13 ternary systems, and 13 higher multicomponent systems, the 2 994 calculated densities agree with the experimental data to within 1.39 percent. For the 2 069 points of data on hydrocarbons and hydro-

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carbon/nitrogen mixtures, the agreement is within 0.95%.

The equation is demonstrated to be suitable for the estimation of pure compound critical volumes. Of the seventy-seven fluids tested, the average absolute error in the estimation of critical volume was 1.64%. For the forty-three hydrocarbons included in this set, the average error was 1.26%.

A generalization of the experimentally based characteristic volumes is presented as a function of acentric factor for each class of compound studied. This adds an additional predictive feature to the correlation.

A useful, general correlation of the volumetric properties of liquids must be applicable to a wide variety of liquids including those for which no experimental data exist. Hence, it must be predictive. It must also, of course, be accurate and reliable. Simplicity, short computation times, convergence properties, and function continuity become very important if a correlation is to be used in a process simulation or a flow computer. Function continuity is important because the presence of a discontinuity in the volumetric property can, in turn, cause difficulties in process calculations.

A correlation for the saturated liquid densities of pure compounds and their mixtures that satisfies the majority of these requirements has been developed; the optimum parameters required for its use were obtained for 200 compounds. The results obtained with this new correlation are compared with those obtained using three well-known correlations.

DATA SOURCES

An extensive literature search was performed to locate saturated liquid density data on both pure compounds and their bubble point mixtures. Reported values which were obtained from charts or nomographs and those which were derived by extrapolation or predictive techniques were excluded from the data base. With few exceptions, all data included in the final data base were obtained from the original sources.

In the LNG and LPG ranges, emphasis was given to data obtained from cooperative industrial and industrial-government research efforts which have been published in recent years. Available data sets on the mercaptans, sulfides, and disulfides were, in some cases, in substantial disagreement. In these cases, new and independent experimental data were obtained, thus allowing reasonable discrimination among the data sets. Additional experimental data were also obtained on several heavy hydrocarbons of general industrial importance.

The final data base used to develop and evaluate the new correlation consisted of 4 508 points of saturated liquid data for 190 pure compounds, and 2 994 points of data for 167 mixtures. The pure compound data set included 2 657 data points for hydrocarbons, 1 303 data points for other organics, and 548 data points for inorganics. The supplement contains the complete reference list for the data base.

AVAILABLE CORRELATIONS

Spencer and Danner (1972) presented a critical review of thirteen correlations for predicting the effect of temperature on the saturated liquid densities of pure fluids. The thirteen correlations studied included those demonstrated by previous review papers to be superior and those techniques published since the earlier reviews. Spencer and Danner demonstrated that of those general purpose correlations based on readily available parameters, the correlations of Yen and Woods (1966), Gunn and Yamada (1971), and Rackett (1970) were the best. In addition, they significantly improved the Rackett equation. This improvement was subsequently included in the American Petroleum Institute Technical Data Book—Petroleum Refining (1972). Their study and development was based on 3 595 points of pure compound data on sixty-four hydrocarbons, thirty-six other organics, and eleven inorganics.

The more important correlations published during or since the study by Spencer and Danner (1972) were developed for specific applications, most often for LNG and LPG calculations, and are not general purpose in formulation. These models are not predictive, are limited in scope because of the temperature range or type of compounds for which they may be used, or present significant size and convergence problems. Of particular note are the models developed for LNG applications (Klosek and McKinley, 1968; Albright, 1973; Yu and Lu, 1976; Diller, 1977; McCarty, 1974; Mollerup and Rowlinson, 1974).

CORRELATION STUDY

In developing this new correlation, we attempted to use the desirable features of the three general purpose correlations recommended by Spencer and Danner (1972) and to eliminate the least desirable ones.

Yen-Woods

The Yen-Woods (1966) equation is

$$V_c/V_s = 1 + A\,(1 - T_R)^{1/3} + B\,(1 - T_R)^{2/3} + (0.93 - B)\,(1 - T_R)^{4/3} \quad (1)$$

where A and B may be determined as specific constants for each compound or may be obtained from generalized functions of Z_c:

$$A = 17.4425 - 214.578Z_c + 989.625Z_c^2 - 1\,522.06Z_c^3 \quad (2)$$

$$B = -3.28257 + 13.6377Z_c + 107.4844Z_c^2 - 384.211Z_c^3 \text{ if } Z_c \leq 0.26 \quad (3)$$

$$B = 60.2091 - 402.063Z_c + 501.000Z_c^2 + 641.030Z_c^3 \text{ if } Z_c > 0.26 \quad (4)$$

Spencer and Danner (1972) have shown that Equation (1) represents pure compound data very well if specific values of A and B for each compound are used. They did not, however, evaluate the results of using the generalized forms of A and B as given by Equations (2), (3), and (4). These generalized forms must be used in conjunction with pseudocritical mixing rules in order to use Equation (1) for mixtures. We find errors of 1.5 to 6.1% when the generalized functions are used for pure hydrocarbons. No mixing rules other than those proposed by Yen and Woods (1966) have been tested. In addition, there is a 3.9% discontinuity between Equations (3) and (4) at $Z_c =$

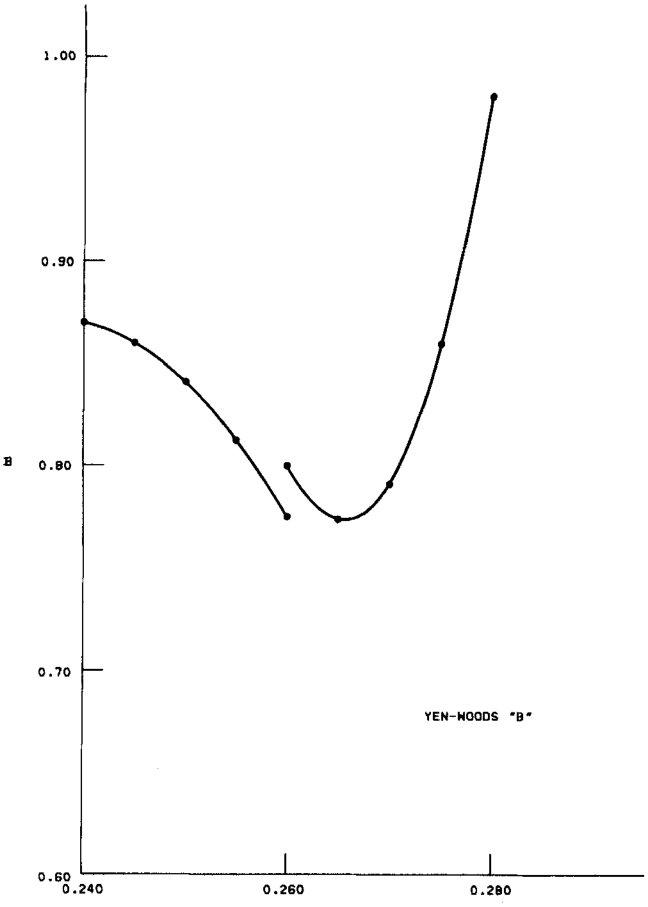

Fig. 1. Plot of the Yen-Woods "B" function.

0.26 which is accompanied by a sharp change in the slope of the curve. These are shown in Figures 1 and 2. This problem would be encountered in a process simulation of a mixture containing both light hydrocarbons through the octane range and heavier hydrocarbons. When the composition of the mixture changes, the Z_c of the mixture will cross the 0.26 value.

Modified Rackett

The equation developed by Rackett (1970) and modified by Spencer and Danner (1972) is

$$V_s = (RT_c/P_c) Z_{RA}{}^{[1+(1-T_R)^{2/7}]} \tag{5}$$

This equation is referred to as the SDR equation in this paper. Z_{RA} is a unique constant for each compound and must be determined from experimental data if the reported accuracy of the equation is to be obtained. If no data are available, Z_c may be used as an estimate of Z_{RA}. The SDR equation is simple and is accurate if experimental values of Z_{RA} are used. A disadvantage is the error introduced by the mixing rules given by Spencer and Danner (1973) and included in the American Petroleum Institute Technical Data Book—Petroleum Refining (chapter 6, 1972). The molar volume of a liquid mixture at its bubble point is given as

$$V_s = V_{cm} Z_{RAm}^{(1-T_R)^{2/7}} \tag{6}$$

where V_{cm} is obtained by the blending of pure compound critical volumes. The ratio of Equation (6), as the limit of composition approaches a pure compound, to Equation (5) results in

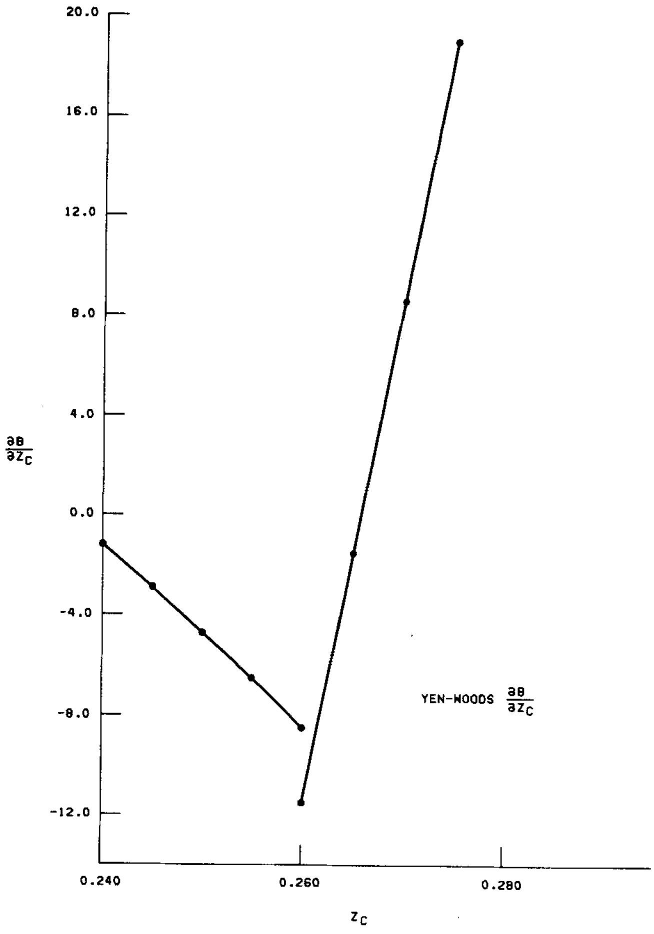

Fig. 2. Slope of the Yen-Woods "B" function.

$$\frac{(RT_cZ_{RA}/P_c)_i}{V_{ci}} \tag{7}$$

Thus, Equation (6) will give the correct limiting result only in the rare instance where $Z_{RA} = Z_c$ and where V_c is based on T_c, P_c and Z_c. Hence, the advantage of the accuracy obtained by using Z_{RA} instead of Z_c will be lost.

Gunn and Yamada

The correlation of Gunn and Yamada (1971), which is claimed to be valid over the reduced temperature range of 0.2 to 0.98, is given by

$$V_s = V_R{}^{(0)} (1.0 - \omega\delta) V_{sc} \tag{8}$$

$$V_{sc} = \frac{V_{0.6}}{0.3862 - 0.0866\,\omega} \tag{9}$$

$$V_R{}^{(0)} = 0.33593 - 0.33953\,T_R - 1.51941\,T_R{}^2 - 2.02512\,T_R{}^3 + 1.11422\,T_R{}^4 \quad \text{if } 0.20 < T_R < 0.80 \tag{10}$$

$$V_R{}^{(0)} = 1.0 + 1.3\,(1 - T_R)^{1/2} \log_{10} (1 - T_R) - 0.50879\,(1 - T_R) - 0.91534\,(1 - T_R)^2 \quad \text{if } 0.80 < T_R < 1.0 \tag{11}$$

$$\delta = 0.29607 - 0.09045\,T_R - 0.04842\,T_R{}^2 \tag{12}$$

The quantity $V_{0.6}$ is a known saturated liquid molar volume at a reduced temperature of 0.6. If an experimental value is known at some other temperature T_{REF}, the equation may be calibrated with the known value V_{REF} and used over the entire valid range of the equation in this form:

$$V_s = (V_{\mathrm{REF}}) \frac{{V_R^{(0)}}^{[1-\omega\delta]}{}_{T_R}}{{V_R^{(0)}}^{[1-\omega\delta]}{}_{T_{\mathrm{REF}}}} \qquad (13)$$

This correlation has the advantage of being dependent on neither V_c nor Z_c. The error in the computed saturated molar volume is directly proportional to the error in the experimental volume used for calibration. A 1% error in the value of V_{sc} will, assuming the validity of the corresponding states correlation, result in a 1% error in the calculated V_s. The SDR equation is, however, more sensitive to the value of its adjustable parameter Z_{RA}. This is demonstrated by an error analysis in which a fractional error ϵ is imposed on the best value of Z_{RA}. The resulting error in calculated volume is

$$\% \text{ error} = 100\,\{1 - (1 \pm \epsilon)^{[1+(1-T_R)^{2/7}]}\} \qquad (14)$$

Table 1 shows the sensitivity of the SDR equation to a 1% error in the value of Z_{RA} at various values of T_R. The resulting error in calculated volume is close to 2% at the lower reduced temperatures.

The Gunn-Yamada equation also has an apparent advantage over the classical linear corresponding states form of Curl and Pitzer (1958):

$$V_R = V_R^{(0)} + \omega V_R^{(1)} \qquad (15)$$

In the Gunn-Yamada correlation, the deviation function $V_R^{(1)}$ is the product of $V_R^{(0)}$ and δ. This product allows the use of a simpler mathematical function for the representation of δ as a function of reduced temperature than is possible with $V_R^{(1)}$. However, the two portions of the $V_R^{(0)}$ function [Equations (10) and (11)] when taken to a reduced temperature of 0.8 have a 0.22% discontinuity in value and a sharp change in slope as shown in Figures 3 and 4. This discontinuity is directly reflected in the calculated V_s. Equation (12), representing the value of the deviation function δ, also shows a discontinuity in that it does not approach zero as the reduced temperature approaches one.

Table 1. Expected Error in Modified Rackett Equation (SDR)

T_R	Exponent	% error in V resulting from a -1.0% error in Z_{RA}
0.2	1.938	−1.95
0.4	1.8642	−1.87
0.6	1.7697	−1.78
0.8	1.6314	−1.64
0.95	1.4249	−1.43

CORRELATION DEVELOPMENT AND TESTING

Based on the analysis of the three correlations, the following model was proposed:

$$\frac{V_s}{V^*} = V_R^{(0)}[1 - \omega_{\mathrm{SRK}} V_R^{(\delta)}] \qquad (16)$$

$$V_R^{(0)} = 1 + a(1 - T_R)^{1/3} + b(1 - T_R)^{2/3} + c(1 - T_R) + d(1 - T_R)^{4/3} \quad 0.25 < T_R < 0.95 \qquad (17)$$

$$V_R^{(\delta)} = [e + f(T_R) + gT_R^2 + hT_R^3]/(T_R - 1.00001) \quad 0.25 < T_R < 1.0 \qquad (18)$$

The model is linear in acentric factor and contains the product of the spherical molecule function $V_R^{(0)}$ and the function $V_R^{(\delta)}$ to represent the deviation function $V_R^{(1)}$. A single adjustable parameter V^*, called the characteristic volume, is required for each pure compound. The terms $V_R^{(0)}$ and $V_R^{(\delta)}$ depend only on reduced temperature and are expressed by functions that contain no mathematical discontinuities. The Yen and Woods form of Equation (1)

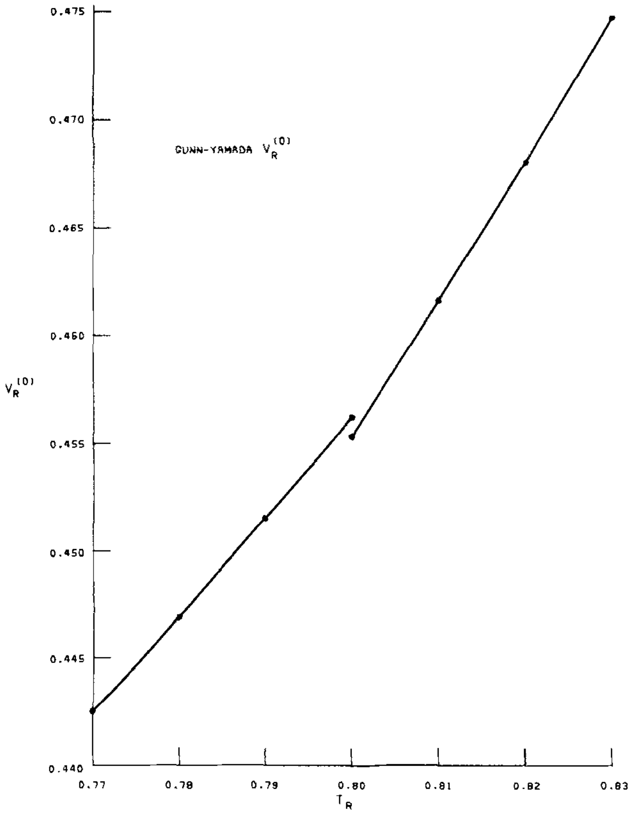

Fig. 3. Plot of the Gunn-Yamada $V_R^{(0)}$ function.

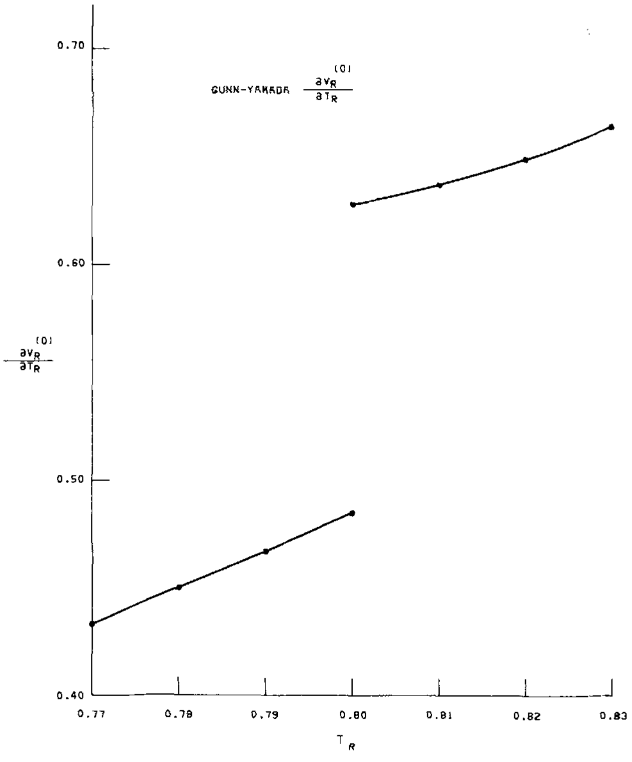

Fig. 4. Slope of the Gunn-Yamada $V_R^{(0)}$ function.

Table 2. Parameters for Equations (17) and (18)

a.	−1.52816
b.	1.43907
c.	−0.81446
d.	0.190454
e.	−0.296123
f.	0.386914
g.	−0.0427258
h.	−0.0480645

is used to represent the spherical molecule function $V_R^{(0)}$ over the entire range of reduced temperatures; this form gives the correct value and slope at the critical point. The $V_R^{(\delta)}$ function becomes asymptotic to one as the critical is approached.

The acentric factor in Equation (16) was given the subscript SRK to denote the source of the values used. As observed by Lee and Kesler (1975), the best set of acentric factors reported to date was published by Passut and Danner (1973) with some revisions by Henry and Danner (1978), but some of their values do not appear to be consistent and their tabulation does not include a number of compounds encountered in hydrocarbon processing. Lee and Kesler (1975) subsequently published a generalized correlation for acentric factor. For similar reasons, in addition to the need to match pure compound vapor pressure data with the equation reported by Soave (1972), we had previously developed a consistent set of acentric factors from current vapor pressure data using the Soave equation of state as the base correlation. At equilibrium, the fugacity of the liquid and the fugacity of the vapor, both obtained from the Soave equation, must be equal. An iterative procedure was used to find the value of acentric factor for each compound that minimized the fractional error between the liquid and vapor fugacities over the range of known vapor pressure data. These values, which are given in Table 6 for 200 compounds, compare very well with those obtained from the Lee and Kesler (1975) correlation.

A limited data set containing values for 190 compounds was selected from the total pure compound data set of 4 508 points for the development of the parameters in Equations (16), (17), and (18) and for the determination of the characteristic volumes. This selection was made based on the source, age, and general acceptability of the data in addition to a trial and error effort to determine the degree of internal consistency between available data sets for the same compound. The final correlation was obtained by a nonlinear regression of all of the selected data to minimize the fractional errors between the calculated and experimental molar volumes. The parameters for Equations (17) and (18) are given in Table 2, while the characteristic volumes for two hundred compounds are given in Table 6.

COMPARISON OF PURE COMPOUND CORRELATIONS

To insure an unbiased comparison between the new correlation COSTALD and the SDR equation, new values of Z_{RA} were obtained from the same data sets used to develop COSTALD. This was done by a nonlinear minimization of the fractional errors between the experimental data and those values calculated from Equation (5). The values of Z_{RA} are given for most of the 200 compounds in Table 6.

The new correlation, the original Yen-Woods correlation, the SDR equation, and, where it applied, the Albright correlation (1973) were tested against the entire 4 508 point data set. A summary of the results by class of compound is given in Table 3. A complete set of comparisons by each data set is given in the supplement and by each compound in Table 6. The table in the supplement also shows which data sets were used to obtain the parameters for both the SDR equation and COSTALD.

Tables 3 and 6 show, that for all pure compounds tested, COSTALD is significantly better than the generalized Yen-Woods equation and generally slightly superior to the SDR equation. They also show that, although no polar compounds were used in their development, both the SDR and COSTALD correlations will fit such data reasonably well.

In a review published after this work was completed, Spencer and Adler (1978) found that with revised parameters, the SDR equation gave slightly better results than the Gunn-Yamada equation and that the Joffe-Zudkevitch (1974) correlation gave poorer results than both the SDR and the Gunn-Yamada equations for hydrocarbons and organics, but better results for associated liquids.

It was not possible to obtain an adequate fit of the pure water data with Equations (16), (17), and (18). However, since it was necessary to have the water correlation in a

Table 3. Saturated Liquid Density Results

Tabular entries average absolute percent error between calculated and experimental

	Paraffins	Olefins and diolefins	Acetylenes	Cycloparaffins	Aromatics
Yen-Woods	1.52	1.52	3.21	6.06	3.08
SDR	0.322	0.311	0.368	0.175	0.181
COSTALD	0.290	0.307	0.392	0.179	0.200
Albright	1.95				

	Fluorocarbons	Cryogenic liquids	Mercaptans	Sulfides	Disulfides
Yen-Woods	1.74	2.81	2.25	2.46	2.23
SDR	0.122	1.62	0.128	0.188	0.147
COSTALD	0.136	0.502	0.119	0.219	0.119
Albright		0.609			

	Condens. gases	Hydroxy compounds	Other organics	Solvents and miscellaneous	Summary all points	
					Avg. absolute percent	Bias
Yen-Woods	1.54	3.87	1.43	2.95	2.141	−4.911
SDR	0.592	2.49	0.259	0.185	0.503	−0.640
COSTALD	0.738	1.70	0.230	0.357	0.374	−0.125

TABLE 4. RESULTS OF THE EVALUATION OF MIXING RULES

Mixing rules case	Average absolute percent error
Aa	1.40
Ab	1.61
Bb	2.96
Ba	2.40
Cb	2.71
Ca	2.15

Case *Ba* gave significantly better results for mixtures of nitrogen with hydrocarbons and hydrogen with hydrocarbons than the other combinations studied.

similar form, both V^* and ω_{SRK} were used as adjustable parameters. For pure water

$$V^* = 43.5669 \text{ cm}^3/\text{g mole}$$

$$\omega_{\text{SRK}} = -0.65445$$

The temperature dependent criticals suggested by Prausnitz and Chueh (1968) were used for hydrogen and helium. Tables 3, 5, and 6 reflect these adjustments for water, hydrogen, and helium.

MIXING RULES

The values of any mixture property obtained from a corresponding states correlation are sensitive to the calculated pseudocritical constants of the mixture. This is especially true for the wide boiling mixtures encountered in the petroleum industry. The use of Kay's simple additive rules (1936) to calculate critical properties of such mixtures lead to significant errors. To improve the overall accuracy of COSTALD, numerous sets of mixing rules, including Kay's rule, were evaluated. The set of mixing rules giving the minimum average absolute percent errors without the use of empirical interaction parameters was selected for use. Interaction parameters may, however, be added for highly accurate work where sufficient precise binary data are available to justify their use. For the general case, the best set of mixing rules is suggested without the use of interaction parameters. In the development of the mixing rules, the characteristic volumes were treated as though they were the pure compound critical volumes. This approach insures that the limits of the correlation are the pure compound values and eliminates the necessity of using uncertain values of critical volume. Of the rules examined, the following combinations gave the most satisfactory results:

A.
$$T_{cm} = \frac{\Sigma_i \Sigma_j \, x_i x_j V_{ij}^* \, T_{cij}}{V_m^*} \tag{19}$$

$$V_m^* = 1/4 \{\Sigma_i \, x_i V_i^* + 3(\Sigma x_i V_i^{*2/3}) \; (\Sigma_i \, x_i V_i^{*1/3})\} \tag{20}$$

$$V_{ij}^* T_{cij} = (V^*_i \, T_{ci} \, V^*_j \, T_{cj})^{1/2} \tag{21}$$

B.
$$T_{cm} = \Sigma_i x_i \, V^*_i \, T_{ci} / \Sigma_i x_i \, V^*_i \tag{22}$$

V^*_m same as above

C.
$$T_{cm} = [\Sigma_i \, x_i \, V^*_i \, (T_{ci})^{1/2}]^2 / (\Sigma \, x_i \, V^*_i)^2 \tag{23}$$

The acentric factors were blended in two ways:

a.
$$\omega_m = \Sigma x_i \, \omega_{\text{SRK}i} \tag{24}$$

b.
$$\omega_m = \frac{\Sigma x_i \, V_i^* \, \omega_{\text{SRK}i}}{x_i \, V_i^*} \tag{25}$$

The results of applying these various rules to the mixture data are shown in Table 4. The combinations of capital and small letters in the table headings indicate the combination of the three sets of T_{cm}, V^*_m rules (A, B, or C) with the two sets of rules for the acentric factor (a or b). The volume average acentric factor, given in Equation (25), resulted in a higher error for the same set of rules for T_{cm} and V^*_m than did the molar average acentric factor, Equation (24). The set of rules designated as Aa and given by Equations (19), (20), (21), and (24) was significantly better than the other rules. This set is recommended for use with COSTALD.

COMPARISON OF CORRELATIONS FOR MIXTURES

The COSTALD correlation with mixing rules given by Equations (19), (20), (21), and (24), the SDR equation with mixing rules suggested by Spencer and Danner (1973), and the Yen-Woods (1966) correlation with pseudocritical constants computed as suggested by the original authors were tested against 2 994 points of liquid mixture data. The results of this comparison are presented in Table 5. The COSTALD correlation exhibits both the lowest percentage error and the minimum bias in all four categories examined. It is significantly better than the SDR equation for the hydrocarbons and hydrocarbon/nitrogen mixtures.

CALCULATION OF CRITICAL VOLUMES

Experimental critical volumes for 77 of the 200 compounds studied were obtained from the compilations of Kudchadker, Alani, and Zwolinski (1968) and Mathews (1972). These are compared with the characteristic volumes listed in Table 6. The results are shown in Table 7. The majority of the characteristic volumes obtained are well within the expected error band of the critical volumes and suggest that the use of COSTALD with experimental saturated liquid density data is a very satisfactory method of estimating pure compound critical volumes.

USE OF COSTALD

COSTALD as given by Equations (16), (17), and (18) along with the parameters presented in Table 2 may be used with a single experimental datum point to obtain the characteristic volume and consequently the entire saturated

TABLE 5. SUMMARY OF MIXTURE

	All data 2 969 pts.		Hydrocarbon mixtures (Includes N_2) 2 069 pts.		At least one hydrocarbon and one nonhydrocarbon 572 pts.		Nonhydrocarbons 328 pts.	
Correlation	% error	bias	% error	bias	% error	bias	% error	bias
Yen-Woods	3.59	−15.6	3.81	−20.8	3.39	−13.9	2.50	14.1
SDR	3.45	−12.09	3.01	−15.92	3.10	−13.75	2.55	14.13
COSTALD	1.39	0.05	0.95	−2.45	2.42	4.95	2.49	5.62

TABLE 6

SUMMARY OF PARAMETERS AND ERRORS FOR INDIVIDUAL COMPOUNDS

	Acentric Factor (SRK)	Char. Volume liter/mole	Z_{RA}	No. of Data Points	AVERAGE ABSOLUTE PERCENT ERROR (1)		
					Yen-Woods	SDR	COSTALD
	PARAFFINS						
Methane	0.0074	0.09939	0.2892	102	0.4750	0.3902	0.4135
Ethane	.0983	.1458	.2808	162	.9258	.1899	.1615
Propane	.1532	.2001	.2766	130	1.3609	.3722	.3412
N-Butane	.2008	.2544	.2730	133	1.2714	.2437	.1962
Isobutane	.1825	.2568	.2754	112	4.9988	.2501	.2191
N-Pentane	.2522	.3113	.2684	123	.9008	.2656	.2310
Isopentane	.2400	.3096	.2717	51	1.1275	.3559	.2914
Neopentane	.1975	.3126	.2756	57	3.3905	.0748	.0603
N-Hexane	.3007	.3682	.2635	112	.8753	.4752	.3195
2-Methylpentane	.2791	.3677	.2672	9	1.1700	.0926	.0982
3-Methylpentane	.2741	.3633	.2690	9	3.3412	.0383	.0579
2,2-Dimethylbutane	.2330	.3634	.2733	5	.5937	.0581	.0699
2,3-Dimethylbutane	.2477	.3610	.2705	13	.1964	.2765	.2596
N-Heptane	.3507	.4304	.2604	62	.4471	.4323	.4462
2,2-Dimethylpentane	.2882	.4225	.2684	22	1.2171	.2591	.1882
2,4-Dimethylpentane	.3040	.4251	.2671	7	1.2944	.0569	.0690
3,3-Dimethylpentane	.2681	.4137	.2707	7	2.2059	.0602	.0851
2,3-Dimethylpentane	.2973	.4127	.2703	7	.8166	1.3461	.8231
2-Methylhexane	.3310	.4274	.2638	8	2.5272	.0966	.1155
3-Methylhexane	.3243	.4231	.2654	5	.7546	.0478	.0601
3-Ethylpentane	.3118	.4163	.2658	22	2.6642	.2562	.1201
2,2,3-Trimethylbutane	.2511	.4125	.2727	8	3.7835	.0586	.0829
N-Octane	.3998	.4904	.2571	66	.3014	.2987	.2071
Isooctane	.3045	.4790	.2684	46	4.6187	.3916	.4336
2,2,3,3-Tetramethylbutane	.2513	.4467	.2738	1	.3866	.006	0.0
N-Nonane	.4478	.5529	.2543	54	.9876	.4925	.4176
N-Decane	.4916	.6192	.2507	44	1.4099	.2620	.1962
N-Undecane	.5422	.6865	.2499	41	1.3784	.1539	.1934
N-Dodecane	.5807	.7558	.2466	39	1.4119	.1380	.2149
N-Tridecane	.6340	.8317	.2473	41	1.8667	.7636	.6455
N-Tetradecane	.6821	.9022	(.2430)	30	.5266	.8715	1.2175
N-Pentadecane	.7254	.9772	(.2418)	18	.7960	.1524	.0986
N-Hexadecane	.7667	1.0539	.2388	14	.6289	.1421	.0884
N-Heptadecane	.7946	1.1208	.2343	40	2.1594	.2076	.3927
N-Octadecane	.8124	1.1989	.2275	30	.9124	1.0657	1.3835
N-Nonadecane	.8328	1.2715	.2236	10	.6680	.0766	.0953
N-Eicosane	.9239	1.3754	.2281	--	(2)	(2)	(2)
Heneicosane	1.0505	1.5081	.2363	4	.7746	.0695	.0207
Docosane	1.0561	1.5839	.2350	4	.7282	.0546	.0291
Tricosane	1.0477	1.6507	.2341	2	1.2654	.1444	.1131
Tetracosane	1.0316	1.7104	--	--	(2)	(2)	(2)
Pentacosane	1.0014	1.7887	--	--	(2)	(2)	(2)
Hexacosane	.9498	1.8133	.2302	2	1.2419	.2164	.0369
Heptacosane	.9001	1.9420	--	--	(2)	(2)	(2)
Octacosane	.8455	1.8972	.2277	3	1.5116	.1167	.0594
	OLEFINS						
Ethylene	.0882	.1310	.2815	45	1.1204	.2917	.2953
Propylene	.1455	.1829	.2779	72	.7154	.3799	.3592
1-Butene	.1921	.2377	.2736	53	2.3644	.5125	.5738
Cis-2-Butene	.2039	.2311	.2701	9	1.2546	.2641	.2238
Trans-2-Butene	.2153	.2367	.2720	31	1.7550	.1757	.1232
Isobutene	.1959	.2369	.2728	35	1.1154	.2110	.2725
1-Pentene	.2824	.2951	.2899	.7	2.5619	.5968	.4505
Cis-2-Pentene	.2426	.2875	.2671	17	3.0606	.6859	.5885
Trans-2-Pentene	.2399	.2929	.2704	4	6.0774	.0514	.0511
2-Methyl-1-Butene	.2355	.2887	.2627	6	1.7668	.0410	.0340
3-Methyl -1-Butene	.2266	.2940	.2739	4	1.6958	.0630	.0655
2-Methyl-2-Butene	.2852	.2883	.2592	4	1.7891	.0601	.0473
1-Hexene	.2850	.3509	.2658	23	1.3136	.1508	.1289
1-Heptene	.3639	.4113	.2611	11	.8791	.2234	.2411
1-Octene	.3876	.4710	.2600	14	.2301	.2690	.2984
1-Nonene	.4327	.5333	.2539	14	3.3000	.2608	.2892
1-Decene	.4975	.6013	.2546	14	1.7775	.1118	.2082
	DIOLEFINS						
Propadiene	.1430	.1655	.2584	1	16.8862	.0001	.0001
1,2-Butadiene	.2492	.2199	.2675	1	.5386	.0003	.0002
1,3-Butadiene	.1934	.2202	.2712	18	.1026	.0707	.0481
1,2-Pentadiene	.1760	.2692	.2677	1	1.6155	.0009	.0000
Isoprene	.1700	.2870	.2652	1	.2077	.0002	.0004
	ACETYLENES						
Acetylene	.2049	.1128	.2709	39	.9518	.2765	.2527
Methylacetylene	.2184	.1609	.2706	16	8.7225	.5926	.7801
Dimethylacetylene	.1581	.2214	.2693	1	5.3996	0.0	.0001
1-Butyne	.0986	.2315	.2711	1	.2208	.0004	.0001

(Continued on next page)

TABLE 6

(Cont.)

CYCLOPARAFFINS							
Cyclopropane	.1305	.1610	.2716	33	8.9675	.0728	.1678
Cyclopentane	.1969	.2600	.2745	13	1.1038	.5053	.5662
Methylcyclopentane	.2322	.3181	.2711	11	1.6278	.0835	.0872
Cyclohexane	.2128	.3090	.2729	24	.8252	.0782	.0638
Methylcyclohexane	.2371	.3709	.2704	36	11.3071	.3126	.2312
1,1-Dimethylcyclopentane	.2691	.3754	.2768	4	1.3916	.0432	.0379
1-Trans-3-Dimethylcyclopentane	.2676	.3796	.2768	4	9.5555	.0443	.0382
1-Trans-2-Dimethylcyclopentane	.2689	.3784	.2763	4	3.1048	.0472	.0415
1-Cis-3-Dimethylcyclopentane	.2825	.3825	.2823	4	3.8814	.0508	.0414
1-Cis-2-Dimethylcyclopentane	.2685	.3706	.2699	4	.9512	.0438	.0409
AROMATICS							
Benzene	.2137	.2564	.2698	58	3.0266	.1436	.2768
Toluene	.2651	.3137	.2644	37	4.4439	.2256	.1852
Ethylbenzene	.3048	.3702	.2620	38	.9290	.2040	.1390
O-Xylene	.3118	.3673	.2625	.8	7.6591	.1371	.1612
M-Xylene	.3216	.3740	.2592	23	.3906	.1880	.2120
P-Xylene	.3216	.3740	.2592	.4	3.5837	.1599	.1331
Styrene	.2420	.3482	.2634	23	.3906	.1880	.2120
Cumene	.3277	.4271	.2617	11	.8229	.0532	.0697
Pentylbenzene	.4406	.5561	.2547	26	6.5817	.2050	.2272
Heptylbenzene	.5441	.6906	.2508	26	3.2242	.1673	.1834
Nonylbenzene	.6583	.8369	.2471	26	1.8704	.2254	.1650
Undecylbenzene	.7659	.9919	.2444	21	1.4642	.2657	.1602
Tridecylbenzene	.9001	1.1693	.2434	19	1.3068	.2973	.2355
Heptadecylbenzene	.9404	1.1456	--	--	(2)	(2)	(2)
Tricosylbenzene	1.1399	1.9952	--	--	(2)	(2)	(2)
Heavy Aromatic	.7619	2.2323	--	--	(2)	(2)	(2)
GASES							
Air	- .0031	.08747	.2962	9	6.6401	1.4709	1.2018
Helium	- .4766	.05457	.2981	11	2.1755	21.1225	4.2571
Hydrogen	- .2324	.06423	.3060	20	5.5496	7.6497	1.3049
Nitrogen	.0358	.09012	.2900	102	.9134	.3399	.2007
Oxygen	.0298	.07382	.2905	69	2.0621	.2255	.2198
GLYCOLS AND AMINES							
Ethylene Glycol	.2280	.2120	.2488	4	1.0255	1.5705	2.9420
Diethylene Glycol	1.0713	.3522	.2489	6	2.4977	2.1422	3.5486
Triethylene Glycol	1.2540	.5347	.2462	8	.2861	.7476	1.1375
Diethanolamine	1.5299	.3143	.2527	1	.2225	.0002	.0002
ALCOHOLS							
Methyl Alcohol	.5536	.1198	.2334	29	1.1018	2.1825	1.6026
Ethyl Alcohol	.6378	.1752	.2502	38	1.7299	2.2683	2.4289
N-Propyl Alcohol	.6249	.2305	.2541	57	1.0534	1.4116	1.6724
Isopropyl Alcohol	.6637	.2313	.2493	26	22.8328	1.6119	1.7928
ALDEHYDES AND KETONES							
Acetaldehyde	.2647	.1519	.2269	5	2.5921	.0863	.0722
Acetone	.3149	.2080	.2477	19	1.1727	.1902	.2978
CHLORINE AND HALIDES							
Chlorine	.0822	.1223	.2767	25	.4279	.3030	.2856
Hydrogen Chloride	.1254	.08383	.2653	18	1.1200	.4491	.8799
ETHERS							
Ethyl Ether	.2800	.2812	.2632	66	1.4594	.2806	.1227
FLUOROCARBONS							
Trichlorofluoromethane	.1871	.2460	.2745	53	2.6184	.1516	.1351
Dichlorodifluoromethane	.1699	.2147	.2757	37	2.9865	.1590	.1982
Chlorotrifluoromethane	.1747	.1807	.2771	54	1.7324	.0913	.0664
Dichloromonofluoromethane	.2102	.1958	.2705	100	1.3204	.0424	.0426
Monochlorodifluoromethane	.2215	.1637	.2663	34	1.5443	.1922	.1715
Trichlorotrifluoroethane	.2560	.3263	.2721	31	1.3397	.1356	.1647
Dichlorotetrafluoroethane	.2582	.2954	.2737	54	1.1668	.1917	.2815
NITROGEN COMPOUNDS							
Ammonia	.2620	.07013	.2465	26	1.1357	.1658	.8162
Hydrazine	.3410	.09844	.2640	30	.3370	.1500	.2010
OXIDES							
Water	.3852	.04357	.2338	104	2.3727	3.5512	1.1605
Carbon Monoxide	.0295	.09214	.2896	46	2.5198	.5986	.4702
Carbon Dioxide	.2373	.09384	.2722	43	1.9218	.2041	.2198
Nitric Oxide	.5896	.05795	.2668	1	9.9565	.0002	.0002
Nitrogen Peroxide	.8634	.09117	.2413	21	1.4799	2.1171	2.1688
Nitrous Oxide	.1691	.09802	.2758	5	.4104	.1660	.1684
Nitrogen Tetroxide	.8573	.09233	.3665	1	5.4281	.1735	.2578
Ethylene Oxide	.2114	.1345	.2569	10	1.1566	.3330	.8873

(Continued on opposite page)

TABLE 6

(Cont.)

SOLVENTS AND MISCELLANEOUS							
Dowtherm A	.4084	.5185	.2542	77	3.0734	.1993	.3902
Sulfolane	.3591	.3136	.2384	8	1.7919	.0503	.0383
SULFUR COMPOUNDS							
Sulfur Dioxide	.2645	.1204	.2661	46	2.3748	.3031	.4408
Sulfur Trioxide	.5025	.1222	.2515	2	8.4643	.1593	.1549
Hydrogen Sulfide	.1039	.09941	.2855	47	.7951	.8012	.8564
Carbon Disulfide	.1035	.1690	.2808	25	4.1175	.5849	.5955
Carbonyl Sulfide	.1021	.1410	.2709	5	8.4049	1.6424	1.9167
MERCAPTANS							
Methyl Mercaptan	.1567	.1508	.2781	4	4.8180	.7252	.7251
Ethyl Mercaptan	.1915	.2023	.2704	21	3.1844	.1204	.2109
N-Propyl Mercaptan	.2380	.2572	.2685	21	2.0845	.1999	.1975
Isopropyl Mercaptan	.2105	.2606	.2810	4	1.8718	.0379	.0378
N-Butyl Mercaptan	.2781	.3135	.2644	22	.7811	.1535	.1520
Sec-Butyl Mercaptan	.2494	.3139	.2731	9	1.6142	.0736	.0705
Isobutyl Mercaptan	.2496	.3159	.2725	4	.4614	.2214	.2216
Tert-Butyl Mercaptan	.1966	.3162	.2831	20	3.0296	.1708	.1222
N-Amyl Mercaptan	.3235	.3728	.2613	9	.8767	.2785	.2764
2-Pentanethiol	.2932	.3709	.2685	13	.5469	.0579	.0384
3-Pentanethiol	.2931	.3676	.2666	3	1.1600	.0442	.0510
Isoamyl Mercaptan	.2935	.3663	.2641	4	.3480	.1923	.1933
3-Methyl-1-Butanethiol	.2934	.3697	.2658	8	.4142	.1831	.2068
Tert-Amyl Mercaptan	.2390	.3674	.2722	9	3.1851	.1185	.1022
Sec-Isoamyl Mercaptan	.2641	.3661	.2698	1	3.8555	.0004	.0002
N-Hexyl Mercaptan	.3726	.4335	.2583	10	1.7394	.0348	.0517
Sec-Hexyl Mercaptan	.3413	.4310	.2646	10	1.1413	.0740	.0265
Tert-Hexyl Mercaptan	.2861	.4233	--	--	(2)	(2)	(2)
Diisopropyl Mercaptan	.2562	.4160	.2664	3	3.5265	.0201	.0237
N-Heptyl Mercaptan	.4253	.4971	.2557	16	2.6171	.0843	.0792
Sec-Heptyl Mercaptan	.3932	.4939	.2614	.0	2.3706	.0965	.0340
N-Octyl Mercaptan	.4808	.5616	.2532	30	2.9644	.0870	.0819
Sec-Octyl Mercaptan	.4477	.5579	.2583	10	3.0771	.0573	.0441
N-Nonyl Mercaptan	.5388	.6301	.2514	12	3.4187	.0979	.0435
Sec-Nonyl Mercaptan	.5048	.6258	.2559	11	3.8425	.1464	.0419
N-Decyl Mercaptan	.5986	.7007	.2493	3	3.2462	.0535	.0594
Sec-Decyl Mercaptan	.5640	.6957	.2534	2	3.8223	.0131	.0015
SULFIDES							
Dimethyl Sulfide	.1936	.2010	.2692	4	1.4806	.0345	.0337
Methyl Ethyl Sulfide	.2435	.2569	.2689	4	2.8866	.0307	.0307
Methyl N-Propyl Sulfide	.2770	.3129	.2653	4	1.2025	.0334	.0331
Diethyl Sulfide	.2938	.3137	.2671	16	4.1999	.2137	.2208
Methyl Isopropyl Sulfide	.2494	.3133	.2728	4	1.5763	.0862	.0861
Methyl N-Butyl Sulfide	.3220	.3716	.2620	4	.1826	.1376	.1378
Ethyl N-Propyl Sulfide	.3250	.3728	.2643	3	.5216	.0356	.0376
Methyl Sec-Butyl Sulfide	.2946	.3715	.2688	3	.1063	.0863	.0971
Methyl Isobutyl Sulfide	.2933	.3705	.2683	3	.2830	.0663	.0762
Ethyl Isopropyl Sulfide	.2940	.3730	.2713	3	.6602	.0400	.0426
Methyl Tert-Butyl Sulfide	.2387	.3666	.2720	3	3.3987	.0415	.0428
Ethyl N-Butyl Sulfide	.3730	.4335	.2611	3	.9526	.0434	.0460
Di-N-Propyl Sulfide	.3741	.4332	.2615	4	.6093	.0330	.0329
N-Propyl Isopropyl Sulfide	.3428	.4328	.2677	2	.1869	.0102	.0009
Ethyl Sec-Butyl Sulfide	.3398	.4288	.2658	2	.6827	.0202	.0125
Ethyl Isobutyl Sulfide	.3421	.4316	.2665	2	.0280	.0166	.0083
Ethyl Tert-Butyl Sulfide	.2848	.4276	.2704	2	3.0580	.0137	.0065
Diisopropyl Sulfide	.3098	.4327	.2747	2	.2575	.0212	.0091
Di-N-Butyl Sulfide	.4824	.5616	.2561	16	2.5304	.1196	.0954
Diisoamyl Sulfide	.6181	.7013	.2589	4	3.3521	.0661	.0305
Diallyl Sulfide	.1031	.3732	.2525	1	5.4906	.0008	.0000
DISULFIDES							
Dimethyl Disulfide	.2610	.2638	.2751	15	2.2289	.0766	.0493
Diethyl Disulfide	.3424	.3803	.2694	20	.6678	.1333	.1112
Ethyl N-Propyl Disulfide	.3876	.4403	.2662	2	.2973	.0161	.0046
Ethyl Isopropyl Disulfide	.3556	.4392	.2711	2	.0783	.0281	.0156
Di-N-Propyl Disulfide	.4391	.5041	.2634	25	1.4054	.1931	.0670
Propyl Isopropyl Disulfide	.4059	.5023	.2680	2	1.1170	.0174	.0038
Ethyl Tert-Butyl Disulfide	.3482	.4950	.2696	2	4.3780	.0266	.0155
Diisopropyl Disulfide	.3734	.4999	.2727	6	1.1865	.0597	.0102
Di-N-Butyl Disulfide	.5507	.6359	.2589	16	2.7114	.1223	.1647
Di-N-Amyl Disulfide	.6707	.7803	.2552	16	3.5844	.0838	.0307
Di-N-Hexyl Disulfide	.7928	.9399	.2525	16	4.4255	.3404	.1052

(1) Average Absolute Percent Error = $\dfrac{\Sigma\left|\left(\dfrac{V_{calc} - V_{exp}}{V_{exp}}\right)\right|}{NP}$

(2) Volumetric Data Not Available or Not Used, V* Computed From Equation (26)

Table 7. Comparison of Experimental Critical Volumes with Characteristic Volumes

Percent difference $= 100(V^* - V_c)/V_c$

Class	Number of compounds	Average absolute percent difference
Paraffins	24	1.62
Olefins	6	1.03
Diolefins	1	0.37
Acetylenes	2	1.03
Cycloparaffins	4	0.35
Aromatics	6	0.89
Gases	9	2.89
Alcohols	4	4.33
Ketones	1	0.46
Chlorine and Halides	2	2.39
Fluorocarbons	7	1.63
Nitrogen compounds	1	3.27
Sulfur containing gases	5	2.89
Mercaptans	2	3.13
Sulfides	2	0.67
Overall average for 77 points		1.64

Table 8. Parameters for Generalized Costald

	Paraffins	Olefins and diolefins	Cycloparaffins	Aromatics	All hydrocarbons
a	0.2905331	0.3070619	0.6564296	0.2717636	0.2851686
b	−0.08057958	−0.2368581	−3.391715	−0.05759377	−0.06379110
c	0.02276965	0.2834693	7.442388	0.05527757	0.01379173
Avg abs. % error	1.23%	1.43%	1.00%	0.58%	1.89%

	Sulfur compds.	Fluorocarbons	Cryogenic liquids	Condensable gases
a	0.3053426	0.5218098	0.2960998	0.2828447
b	−0.1703247	−2.346916	−0.05468500	−0.1183987
c	0.1753972	5.407302	−0.1901563	0.1050570
Avg abs. % error	1.98%	0.82%	0.85%	3.65%

liquid density curve for fluids not covered in Table 6. Often, however, the single datum point required is not readily available. Consequently, to provide a predictive capability for such cases, the characteristic volumes have been correlated with the following expression:

$$V^* = \frac{RT_c}{P_c}(a + b\omega_{SRK} + c\omega^2_{SRK}) \tag{26}$$

Table 8 presents the values of the constants *a, b,* and *c* for nine classes of fluids. Since the expected error in calculated volume or density is directly proportional to the error in characteristic volume, the average percent errors given for each class in Table 8 also represent the anticipated errors in calculated volumetric properties. Thus, the Table 8 parameters and Equation (26) should never be used in preference to characteristic volumes obtained from reliable experimental data. However, the results obtained by their use will, on the average, be superior to those obtained from the generalized Yen-Woods correlation.

Recent comparison of COSTALD with McCarty's (1977) modification of the Klosek-McKinley method* (for $C_1 - C_5$ paraffins and nitrogen, 95° to 150°K) gave for 222 pure liquid points, COSTALD: 0.202%, McCarty: 0.283% average absolute error, and for 370 mixture points, COSTALD: 0.291%, McCarty: 0.446% error. COSTALD biases were slightly smaller also.

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NOTATION

A,B = Yen-Woods constants, Equations (1) to (4)
a,b,c = constants as given in Table 8 and Equation (26)
P_c = critical pressure
R = gas constant
SDR = Rackett equation as modified by Spencer and Danner
T_c = critical temperature
T_{cm} = critical temperature of mixture
T = temperature, absolute
T_R = reduced temperature, T/T_c
V_c = critical volume
V_{cm} = critical volume of mixture
$V_R^{(0)}$ = corresponding states function for normal fluids
$V_R^{(1)}$ = corresponding states deviation function
$V_R^{(\delta)}$ = deviation function for new correlation
V_s = saturated liquid volume
V_{sc} = Gunn-Yamada scaling volume, Equation (9)
V^* = characteristic volume, l/mole
V_m^* = characteristic volume of mixture
Z_c = critical compressibility factor
Z_{RA} = SDR Z factor
Z_{RAm} = SDR Z factor of mixture
δ = Gunn-Yamada deviation functions
ω = acentric factor
ω_{SRK} = acentric factor from the Soave equation of state
ω_m = acentric factor of mixture

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Theoretical Prediction of Effective Heat Transfer Parameters in Packed Beds

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A theory for predicting the effective axial and radial thermal conductivities and the apparent wall heat transfer coefficient for fluid flow through packed beds is derived from a two-phase continuum model containing the essential underlying and independently measurable heat transfer processes. The theory is shown to explain much of the confused literature and pinpoints the remaining major areas of uncertainty, further investigation of which is needed before secure prediction is possible.

SCOPE

Knowledge of the effective thermal conductivity and wall heat transfer coefficient for fluid flow through packed tubular beds forms an important aspect in the design of catalytic reactors.

In studying heat transfer in packed beds, we attempt to answer the following question: Given the mass velocity of the fluid, the mean bed voidage, the tube diameter, the particle size, shape and conductivity, and the essential physical properties of the fluid such as the viscosity, specific heat, and molecular conductivity, what values do the effective axial and radial conductivity of the bed and the wall heat transfer coefficient take? This question has dogged researchers for the past 25 yr, and, despite the vast literature, no satisfactory answer has been found. Nor will it be answered, we believe, by producing yet more empirical correlations.

The main objective of this paper and contribution to the profession, we hope, is to direct attention towards a theoretical, rather than empirical, approach. By theoretical approach, we imply the development of a model relating effective heat transfer parameters to the essential underlying and independently measurable heat transfer processes. Thus, no empirical or adjustable constants are involved. We have accounted for seven such basic heat transfer steps which we have felt necessary to review in the middle part of our paper.

The predictions of the theory are compared with reliable literature data for qualitative trends in parameter relations as much as for absolute accuracy. We feel that a thorough testing of our theory must await further experimental work on several of the basic heat transfer steps.

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