TABLE VI. CORRELATIONS OF CRITICAL PRESSURE

Compound	Experimental, P_c, atm.	Authors' Correlation P_c, atm.	Authors' Correlation Dev., %	Lydersen P_c, atm.	Lydersen Dev., %
Propylene oxide	48.6	49.10	1.03	51.40	5.76
Diethyl ether	35.6	37.52	5.39	37.39	5.03
Vinyl ethyl ether	40.2	39.26	-2.34	39.56	-1.59
1,2-Dimethoxyethane	38.2	35.59	-6.83	36.66	-4.03
Isopropyl ether	28.4	29.54	4.01	30.58	7.68
		Av. Deviation	3.92%		4.82%
Furan	52.5	51.32	-2.25	58.79	11.98
2-Methylfuran	46.6	45.93	-1.44	48.35	3.76
Tetrahydrofuran	51.2	53.92	5.31	50.41	-1.54
2-Methyltetrahydrofuran	37.1	44.46	19.84	42.06	13.37
Pyrrolidine	56.3	57.74	2.56	48.48	-13.89
Pyridine	55.6	56.42	1.47	51.43	-7.50
Thiophene	56.2	49.38	-12.14	58.83	4.68
Dioxane	51.4	47.74	-7.12	50.87	-1.03
		Av. Deviation	6.52%		7.22%

Equation 13 gives average and maximum deviations only slightly greater than those given by the equation

$$P_c = a/M + b \tag{14}$$

used by Kobe and coworkers (11) for ketones. Equation 14 gave poor correlations for the critical pressures of ethers and heterocyclics.

Table VI compares experimental values, correlations by equations 10 and 11, and Lydersen's correlation.

The correlations developed here are of the form usually applied to homologous series. The ethers and heterocyclics tested cannot be regarded as members of such series; therefore, these correlations are less accurate than those which might be developed if critical properties of several members of an homologous series were known. Group contribution methods seen most promising. Lyderson states that many of his group contributions are based on insufficient data for accuracy. More experimental data, as given here, should improve this method.

ACKNOWLEDGMENT

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REFERENCES

(1) Fair, J. R., Lerner, B. J., AIChE J. 2, 13-17 (1956).
(2) Fischer, R., Reichel, T., Mikrochemie 31, 102 (1943).
(3) Gamson, B. W., Chem. Eng. Progr. 45, 154 (1949).
(4) Grunberg, L., J. Chem. Phys. 22, 157 (1954).
(5) Herz, W. Von, Neukirch, E., Z. Physik. Chem. 104, 433 (1923).
(6) Hojendahl, K., Kg. Danske Vindenskab Selskab, Mat-fys., 24, No. 2, 1 (1946).
(7) Hougen, O. A., Watson, K. M., Ragatz, R. A., "Chemical Process Principles," Pt. I, pp. 87-97, Wiley, New York, 1954.
(8) Ipatieff, V. N., Monroe, G. S., Ind. Eng. Chem., Anal. Ed. 14, 171 (1942).
(9) Kobe, K. A., Lynn, R. E., Jr., Chem. Revs. 52, 123 (1953).
(10) Ibid., p. 113.
(11) Kobe, K. A., Crawford, H. R., Stephenson, R. W., Ind. Eng. Chem. 47, 1767 (1955).
(12) Lydersen, A. L., Rep. 3, Engineering Experiment Station, Univ. of Wisconsin, April 1955.
(13) Meissner, H. P., Redding, E. M., Ind. Eng. Chem. 34, 521 (1942).
(14) Nelson, L. G., Obert, E. F., AIChE J. 1, 74 (1955).
(15) Nelson, L. G., Obert, E. F., Chem. Eng. 61, No. 7, 203-8 (1954).
(16) Pawlewski, B., Ber. 21, 2141 (1888).
(17) Radice, doctoral thesis, Geneve, 1899; Bornstein Landolt, Tabellen, vol. 1, p. 256, Springer, Berlin, 1923.
(18) Riedel, L., Z. Elektrochem. 53, 222 (1949).
(19) Riedel, L., Chem. Ing. Tech. 24, 353 (1952).
(20) Schiff, R., Ber. 18, 1601 (1885).
(21) Schroer, E., Z. Physik. Chem. 140, 240 (1929).
(22) Ibid., p. 379.
(23) Uyehara, O. A., Watson, K. M., Natl. Petroleum News, Tech. Sec. 36, R764 (1944).
(24) Varshni, Y. P., J. Chem. Phys. 21, 2235 (1953).

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Benedict Equation of State

Methane-n-Pentane System

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Equations of state find industrial application in predicting the thermodynamic properties of fluids.

Coefficients for the Benedict equation of state were determined by least squares methods from experimental data for mixtures of the methane-n-pentane system. Values were obtained for the interaction constants for groupings of the Benedict coefficients corresponding to the second and third virial coefficients.

In the liquid and gas phases at pressures up to 5000 pounds per square inch between 100° and 460° F. the accuracy of description of the volumetric behavior was improved severalfold by use of interaction constants evaluated by least squares methods over constants calculated by the method suggested by Benedict. Such methods may prove useful in evaluating interaction constants for mixtures as a function of the characteristics of the system involved.

Benedict, Webb, and Rubin (3-7) developed an empirical equation of state which describes the volumetric behavior of gaseous hydrocarbons with satisfactory accuracy at pressures up to 4000 pounds per square inch and gives a good prediction of the phase behavior of many hydrocarbon mixtures. Brough, Schlinger, and Sage (8) proposed an analytical method based on least squares techniques for evaluating the coefficients, which extended earlier proposals of Benedict (2). Selleck, Opfell, and Sage (15) extended the application of this equation for propane to pressures up to 10,000 pounds per square inch in the temperature interval between 40° and 460° F. and included a description of the behavior of the liquid phase. Similarly Opfell (12, 13) evaluated coefficients of the Benedict equation for nine of the lighter hydrocarbons from methane through n-decane for describing the volumetric behavior in both the liquid and gas phases for the range of pressures and temperatures covered by Selleck (15). The coefficients suggested by

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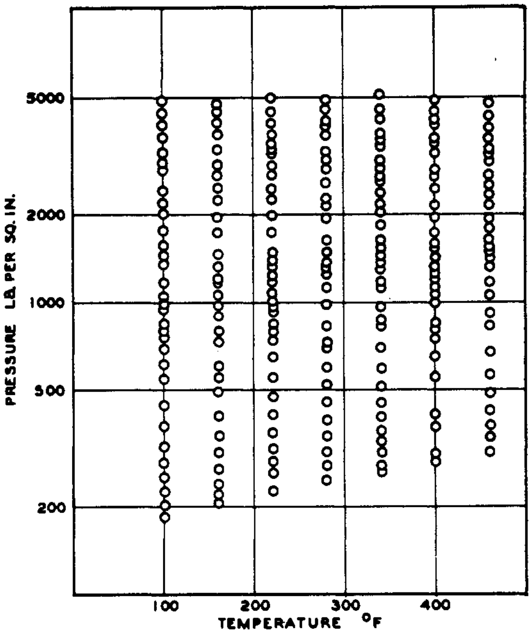

Figure 1. Experimental data used to establish coefficients for a mixture containing 0.9822 mole fraction methane

Selleck (15) and Opfell (12, 13) are suitable only for the prediction of the volumetric behavior, whereas the coefficients suggested by Benedict, while they are of primary utility in describing the volumetric behavior of the gas phase at lower pressures, are suitable for estimation of phase behavior as well.

For present purposes the Benedict equation may be written with pressure or compressibility factor as explicit functions of temperature and volume. The latter form of the equation may be written in the following way:

$$Z = \frac{PV}{RT} = 1 + \left[B_0 - \frac{A_0}{RT} - \frac{C_0}{RT^3}\right]\frac{1}{V} + \left[b - \frac{a}{RT}\right]\frac{1}{V^2} + \frac{a\alpha}{RT}\frac{1}{V^5} + \frac{c}{RT^3}\left(\frac{1}{V^2} + \frac{\gamma}{V^4}\right)\exp\left(-\frac{\gamma}{V^2}\right) \quad (1)$$

In applying the equation to one-component system, the values of the coefficients A_0, B_0, C_0, a, b, c, α, and γ are found to be characteristic of the substance. The values of the coefficients for a multicomponent system would vary in a regular fashion with composition and would approach the values of the coefficients for the individual components as the respective mole fraction approach unity. Little has been reported concerning computation of coefficients from experimental data for mixtures. The application of the equation to multicomponent systems has for the most part (3) depended on coefficients obtained by averaging the coefficients of the constituents of the mixture.

Benedict's extension (3, 4, 6) of the equation to mixtures was based on two primary assumptions. The coefficients for the mixture were described as specific continuous functions of composition involving the coefficients for the components and a set of interaction constants.

$$A_0 = \eta_i^2 A_{0i} + 2\eta_i\eta_j A_{0ij} + \eta_j^2 A_{0j} \quad (2)$$

$$b = \eta_i^3 b_i + 3\eta_i^2\eta_j b_{iij} + 3\eta_i\eta_j^2 b_{ijj} + n_j^3 b_j \quad (3)$$

In Equations 2 and 3, the single-subscript symbols-A_{0i}, A_{0j}, b_i, b_j,-are the coefficients for the components. The double- and triple-subscript symbols- A_{0ij}, b_{iij}, b_{ijj}-are the interaction constants. These mixture coefficients become equal to the coefficient for a given molecular species when its mole fraction equals unity.

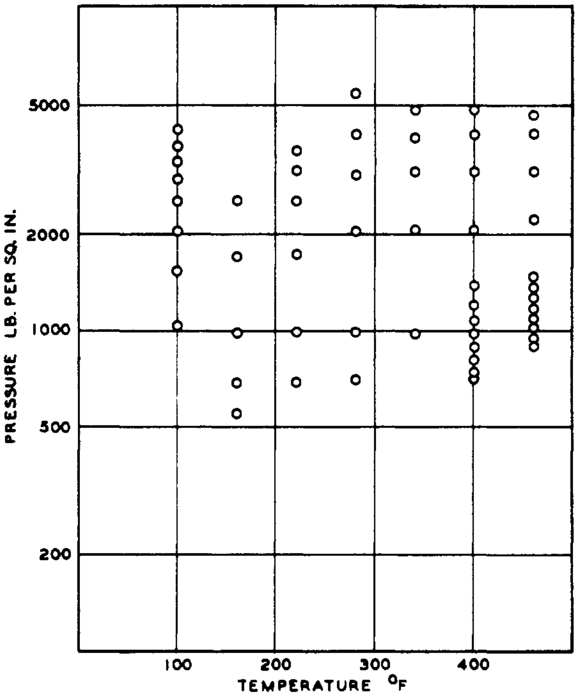

Figure 2. Experimental data used to establish coefficients for a mixture containing 0.1263 mole fraction methane

Benedict's second assumption was that the interaction constants could be satisfactorily approximated by averaging the coefficients of the components. Two general types of expressions were suggested,

$$A_{0ij} = [A_{0i}A_{0j}]^{1/2} \quad (4)$$

$$b_{iij} = [b_i b_i b_j]^{1/3} \quad (5)$$

In later work (7) Benedict apparently preferred a linear average for B_{0ij}.

Benedict's first assumption is suggested by comparison of his equation with the virial equation of state predicted by statistical mechanical analysis of a system of particles with intermolecular potential functions. The single-subscript constants in this analysis represent interaction of molecules of the same type, whereas double- and triple-subscript constants correspond to interactions between unlike molecules (10). The second assumption, which suggests an approximation for the interaction constants, has no apparent foundation in theory or from experimental data, although it has yielded results that have proved useful (3, 4, 7).

Guggenheim (9) computed the interaction constants for six binary gaseous systems at low pressures and showed that for these systems the constants may be predicted with fair accuracy from a universal reduced second virial coefficient determined by data from pure substances. Hirschfelder, Curtiss, and Bird (10) suggested semiempirical methods of predicting the equivalent of interaction constants which should be suitable for application at low pressures. Beattie and Stockmayer (1) investigated a variety of methods of predicting the interaction constants of the second virial coefficients for the gaseous methane-butane system. Recently Stotler and Benedict (17) indicated that an empirical adjustment of the interaction constant

TABLE I. CONSTANTS OF BENEDICT EQUATION FOR METHANE AND n-PENTANE[a]

Constant	Methane	Pentane
R	10.73147[b]	10.73147
$A_0 \times 10^{-3}$	4.91053	60.2155
B_0	0.455158	3.69003
$C_0 \times 10^{-9}$	0.448753	19.6289
$a \times 10^{-3}$	4.55118	203.9410
b	1.03508	16.0875
$c \times 10^{-9}$	0.619147	116.0610
α	0.332260	6.67703
γ	1.200000	10.50000
M	16.042	72.146

[a] (14).

[b] Values recorded are dimensionally consistent when used in the equation of state with pressures expressed in pounds per square inch, temperature in degrees Rankine, and volume in cubic feet per lb.-mole. Absolute temperature at ice point was taken as 459.69° R.

A_{012} for the nitrogen-methane system materially increased the accuracy of the description by the Benedict equation.

The present discussion describes the application of least squares methods to the evaluation of mixture coefficients and selected interaction constants in the Benedict equation of state for the methane-n-pentane system. The mathematical procedures employed were similar to those described by Brough (8) and extended by Selleck (15, 16), and no details of the extended calculations associated with this work are presented here. The program was divided into three steps. First, independent sets of coefficients were obtained for each of six mixtures. Secondly, the data for all six mixtures were used in the computation of the interaction constants associated with the coefficients A_0, B_0, and C_0. Finally, the interaction constants associated with A_0, B_0, C_0, a, b, and c were computed simultaneously.

EXPERIMENTAL DATA

The experimental data for the methane-n-pentane system were based on an experimental investigation (14) which extended to a pressure of 5000 pounds per square inch in the temperature interval between 100° and 460° F. The study included six mixtures varying from 0.03 to 0.92 weight fraction methane. All the experimental data involving states in the heterogeneous regions were excluded, leaving a total of 733 states in the homogeneous regions. Of this total, 132 states were in the liquid phase. For simplicity of description the term "liquid" will indicate a state below that corresponding to the critical temperature and a pressure in excess of the bubble-point pressure. A representative sample of the experimental points employed in this investigation is presented upon the temperature-pressure diagram of Figures 1 and 2.

The coefficients used for methane and n-pentane were those recently obtained by Opfell (13). They were based upon values of γ giving the best volumetric description of the experimental data. The coefficients for methane were based upon experimental data extending up to 10,000 pounds per square inch in the temperature interval between -100° and 500° F. The coefficients for n-pentane were limited to temperatures between 100° and 460° F. and to pressures up to 10,000 pounds per square inch. The values of the coefficients employed are recorded in Table 1 for the convenience of the reader.

COEFFICIENTS FOR INDIVIDUAL MIXTURES

In order to establish nearly the minimum deviations to be expected with the Benedict equation of state in describing the volumetric behavior of the mixtures (14), the coefficients with the exception of γ for each of the six individual mixtures were established. The values of γ were deter-

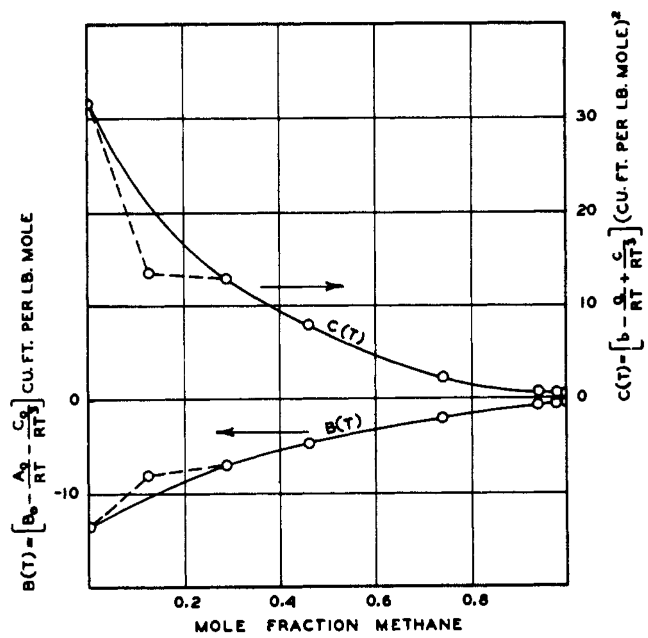

Figure 3. Effect of composition upon coefficients of Benedict equation at 160° F.

TABLE II. CONSTANTS OF BENEDICT EQUATION FOR SIX MIXTURES

Constant	Mole Fraction Methane 0.9822	0.9404	0.7385	0.4636	0.2933	0.1263
$A_0 \times 10^{-3}$	9.681615	5.714402	11.284436	21.086886	30.299301	37.106893
B_0	0.976771	0.589944	0.883116	1.141549	1.400853	1.081886
$C_0 \times 10^{-9}$	0.133002	1.096448	3.204144	7.193561	9.773934	9.612066
$a \times 10^{-3}$	-6.771065	6.653650	17.384449	77.513929	133.381453	192.036492
b	-0.092306	1.138778	2.453100	7.753380	12.571227	18.809025
$c \times 10^{-9}$	-0.629810	1.656143	6.855081	30.225136	52.155148	59.837555
α	0.006639	0.538037	1.224530	1.965381	2.838144	3.694810
γ	1.284958[a]	1.496238	2.743651	5.044583	6.818292	8.817651
Root-mean-square error	0.0073	0.0039	0.0056	0.0043	0.0113	0.0098

[a] Values for γ were obtained from Equation 6.

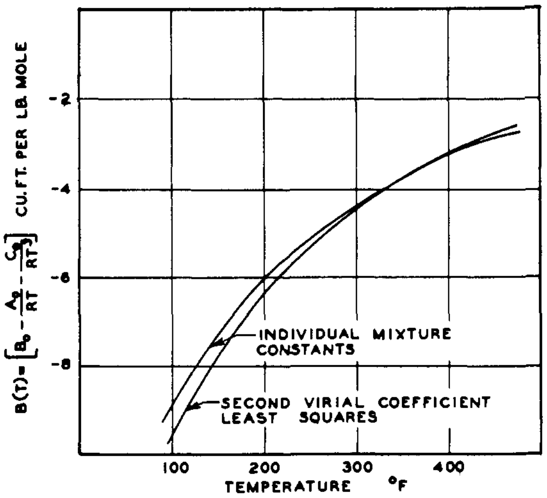

Figure 4. Second virial coefficient for a mixture of methane and n-pentane containing 0.2933 mole fraction methane

mined in accordance with Benedict's suggestion (4, 6) as indicated in the following expression:

$$\gamma = \eta_1^2\gamma_1 + 2\eta_1\eta_5[\gamma_1\gamma_5]^{1/2} + \eta_5^2\gamma_5 \qquad (6)$$

Values for each of the other coefficients were established by determining the sets which minimized the sum of the squares of the residuals in compressibility factor, with temperature and volume as the independent variables. The unsmoothed, unweighted experimental data (14) were employed for this evaluation. The results are shown in Table II. The root-mean-square error in the compressibility factor with volume and temperature as the independent variables was 0.00705. The average relative error in pressure which is defined by the following expression was 0.00461:

$$\epsilon_P = \frac{1}{N}\sum_1^N \frac{|P_e - P|}{P} \qquad (7)$$

For many applications the error in volume with pressure and temperature as the independent variables is more indicative of the utility of the equation. The relative error in volume at each state was estimated from

$$\frac{V_e - V}{V} \cong \frac{P_e - P}{P}\frac{P}{V}\left(\frac{\partial V}{\partial P}\right)_{T,n_i} \qquad (8)$$

The values of the derivative of volume with respect to pressure at constant temperature and composition were computed from the Benedict equation. The average relative error in volume, which is defined by the following expression, was estimated to be 0.00298:

$$\epsilon_V = \frac{1}{N}\sum_1^N \frac{|V_e - V|}{V} \qquad (9)$$

TABLE III. INTERACTION CONSTANTS OF BENEDICT EQUATION

	Benedict Linear	Benedict Square Root	Least Squares: 2nd virial coefficient	Least Squares: 2nd and 3rd virial coefficients
γ_{15}	3.549648[a]	3.549648	3.549648	3.549648
α_{115}	0.903330	0.903330	0.903330	0.903330
α_{155}	2.455923	2.455923	2.455923	2.455923
B_{015}	2.072593	1.295973	0.745524[b]	0.615646
$A_{015} \times 10^{-3}$	17.195641	17.195641	10.277994	12.462433
$C_{015} \times 10^{-9}$	2.967918	2.967918	3.169343	1.659504
b_{115}	2.583128	2.583128	2.583128	3.474415
b_{155}	6.446390	6.446390	6.446390	7.900746
$a_{115} \times 10^{-3}$	16.165302	16.165302	16.165302	18.427891
$a_{155} \times 10^{-3}$	57.417496	57.417496	57.417496	69.183760
$c_{115} \times 10^{-9}$	3.543440	3.543440	3.543440	1.017588
$c_{155} \times 10^{-9}$	20.279449	20.279449	20.279449	20.031450
Root-mean-square error	0.0575	0.0408	0.0122	0.0106
Av. $\frac{1}{P}\lvert\Delta P\rvert$	0.0563	0.0294	0.0108	0.0092
Av. $\frac{1}{V}\lvert\Delta V\rvert$	0.0325	0.0124	0.00664	0.00541

[a] See footnote b of Table I concerning units.

[b] In the two least squares cases, the underlined values are the result of the computations. The values for the other constants in these two columns are based on Benedict's approximations.

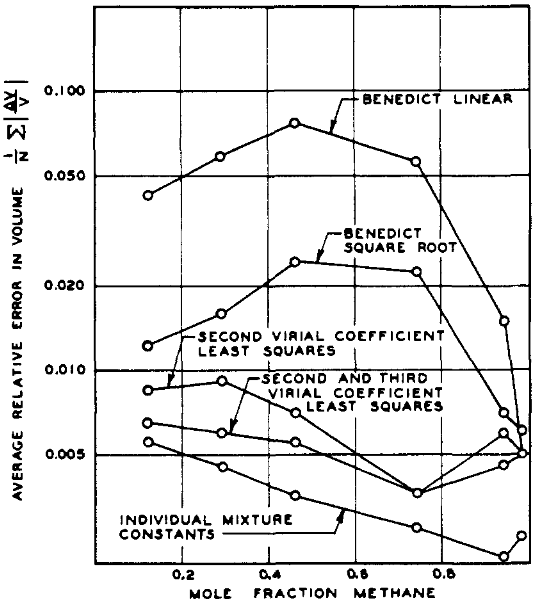

Figure 5. Average relative error in volume as a function of composition

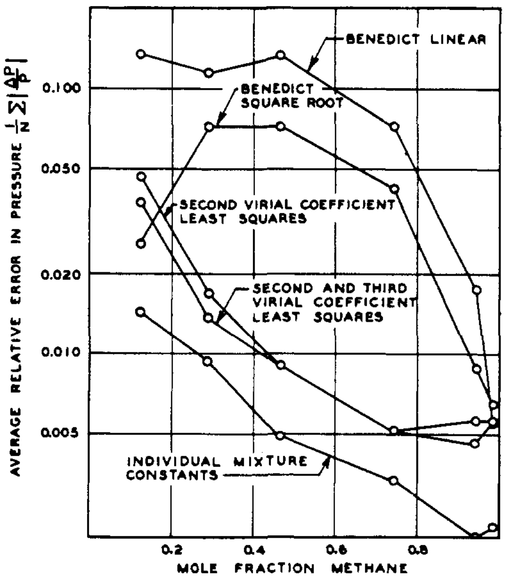

Figure 6. Average relative error in pressure as a function of composition

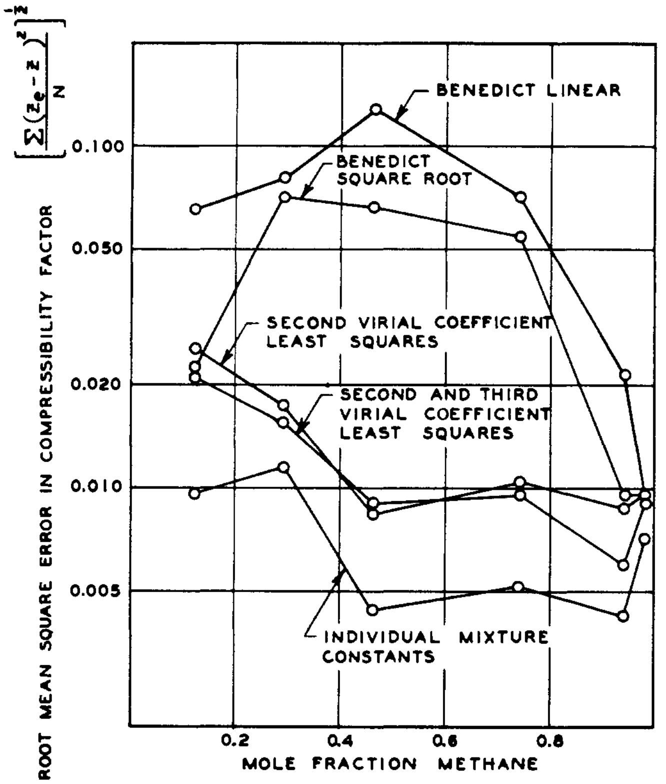

Figure 7. Root-mean-square error in compressibility factor as a function of composition

A more detailed review of the accuracy of agreement of the Benedict equation with the coefficients evaluated for each mixture is set forth in a part of Table II. The deviations indicated for each individual mixture represent the minimum deviations to be expected with the continuous variation in γ employed. Mixture coefficients which are the continuous functions of composition will yield deviations from the experimental data which are at best equal to those recorded in Table II. The variations in several of the coefficients with composition are shown in Figure 3. The experimental data yield rather smooth variations in the coefficients with composition, except for the mixture near 0.12 mole fraction methane. This mixture appears to deviate markedly from the behavior found for the other mixtures. As these coefficients are not continuous functions of composition, they do not permit the equation to be used to obtain partial thermodynamic properties (11), to obtain deviatives with respect to composition, or to interpolate with respect to composition.

EVALUATION OF INTERACTION CONSTANTS

As a guide to the study of the interaction constants, the Benedict equation was compared with the virial equation of state by expanding the exponential term of Equation 1 in a power series.

$$Z = 1 + \left[B_0 - \frac{A_0}{RT} - \frac{C_0}{RT^3}\right]\frac{1}{V} + \left[b - \frac{a}{RT} + \frac{c}{RT^3}\right]\frac{1}{V^2} + \frac{a\alpha}{RT}\frac{1}{V^5} + \frac{c\gamma^2}{RT^3}\left(\frac{1}{2!} - \frac{1}{1}\right)\frac{1}{V^6} + \frac{c\gamma^3}{RT^3}\left(\frac{1}{2!} - \frac{1}{3!}\right)\frac{1}{V^8} + \ldots\ldots \quad (10)$$

Expressed in this form, the term involving the coefficients A_0, B_0, and C_0 is seen to be similar to the second virial coefficient, whereas the term involving b, a, and c is similar to the third virial coefficient. In keeping with this analogy, these groupings are referred to as the second and third virial coefficients of the equation, and it is borne in mind that the preassigned form of the equation may result in poor approximation to the virial coefficients of a substance predicted by other means. Benedict's expressions similar to Equations 2 and 3 for the coefficients may be substituted in Equation 1, resulting in an equation of state with twelve interaction constants. For the interaction constants involved in the coefficients ($a\alpha$) and γ, which appear only in the higher order terms of the virial analogy given in Equation 10, the approximations of Benedict (2) presented for γ in Equation 6 were assumed to be adequate.

In order to evaluate the remaining nine interaction constants, two separate approaches were employed. In the first the suggestions of Benedict (6) typified by Equation 5 were assumed to be adequate for the terms appearing in the third virial coefficient. A least squares solution was found for A_{015}, B_{015}, and C_{015}, which appear in the second virial coefficient. In the second evaluation, the least squares solution was found for all nine of the interaction constants in the second and third virial coefficients. Since the constants of the equation are interdependent, the values obtained for A_{015}, B_{015}, and C_{015} would not be expected

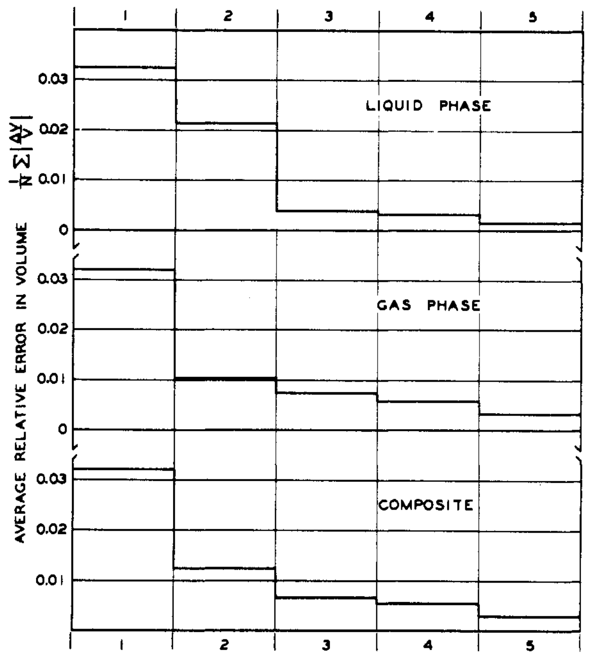

Figure 8. Average relative error in volume for several sets of coefficients

Column 1. Benedict's interaction constants. Linear combination for B_{015}

Column 2. Benedict's interaction constants. Square root combination for B_{015}

Column 3. Least squares interaction constants. A_{015}, B_{015}, C_{015}, by least squares; a_{115}, a_{155}, b_{115}, b_{155}, c_{115}, c_{155}, α_{115}, α_{155}, γ_{15} by Benedict functions

Column 4. Least squares interaction constants. A_{015}, B_{015}, C_{015}, a_{115}, a_{155}, b_{115}, b_{155}, c_{115}, by c_{155}, by least squares; α_{115}, α_{155}, γ_{15} by Benedict functions

Column 5. Individual mixture constants

TABLE IV. INFLUENCE OF INTERACTION CONSTANTS ON ERROR OF PREDICTION

	Least Squares Coefficients for Individual Mixtures	Benedict Interaction Constants		Least Squares Interaction Constants	
		B_{015} linear	B_{015} square root	2nd virial coefficient	2nd and 3rd virial coefficients
Root-mean-square error in Z					
Gas	0.0060	0.0472	0.0171	0.0093	0.0081
Liquid	0.1055	0.0908	0.0889	0.0207	0.0185
Total	0.0070	0.0575	0.0407	0.0122	0.0107
Average $\frac{1}{P}\lvert\Delta P\rvert$					
Gas	0.0033	0.0377	0.0125	0.0076	0.0062
Liquid	0.0104	0.1411	0.1060	0.0254	0.0227
Total	0.0046	0.0563	0.0294	0.0108	0.0092
Average $\frac{1}{V}\lvert\Delta V\rvert$					
Gas	0.0033	0.0324	0.0104	0.0072	0.0059
Liquid	0.0017	0.0325	0.0215	0.0040	0.0034
Total	0.0030	0.0325	0.0124	0.0066	0.0054

to be the same in the two methods of evaluation. In both cases the entire data set covering mixtures of six different compositions and a total of 733 points was employed. Interaction constants were determined by minimizing the sum of the squares of the residuals in compressibility factor with temperature, molal volume, and mole fraction as the independent variables.

The results of the calculations for the interaction constants of the second virial coefficient are shown in Table III. The second virial coefficient is plotted as a function of temperature in Figure 4. For comparison, the values of the interaction constants predicted by Benedict's suggestions have been included. The values of γ, $a\alpha$, and the third virial coefficient were determined by the methods suggested by Benedict (6). Under these circumstances an average relative error in volume of 0.66% was obtained, as compared to 1.2% for the prediction involving Benedict's interaction constants to establish the coefficients. If, on the other hand, a linear average is employed for B_o, as suggested by Benedict, the average relative error in molal volume is 3.2%.

Figure 5 depicts the average relative error in volume, with pressure and temperature as the independent variables at fixed composition. This diagram indicates that Benedict's interaction constants for the second virial coefficient yield relatively large errors near the center of the composition interval, whereas the least squares method of evaluation of the interaction constants for the second virial coefficent yields roughly a uniform average relative error in volume throughout the composition interval. None of the curves in Figure 5 has been extended to pure methane or to pure pentane. Under the second set of circumstances, it was necessary to solve for a total of nine constants-B_{015}, A_{015}, C_{015}, b_{115}, b_{155}, a_{115}, a_{155}, c_{115}, and c_{155}. The corresponding second virial coefficient is shown in Figure 3 as a function of temperature. The average relative error in volume was 0.54%, as compared to 0.66% with only the second virial coefficient established by least squares methods. In the case of the empirical evaluation of the coefficients for each mixture the average relative error was 0.29%. It appears possible to describe the volumetric behavior of mixtures, with the combining functions typified by Equations 2 and 3, with an uncertainty only about twice as large as that found with the use of the Benedict equation to describe the volumetric behavior of each individual mixture. There is shown in Figure 5 the behavior when both the second and third virial coefficients are evaluated by least squares techniques. In this instance the average error is relatively uniform throughout the composition interval and is only slightly greater than that obtained with the individual evaluation of the coefficient for each mixture.

Figure 6 depicts the average error in pressure, with volume and temperature as the independent variables, for each of the several methods of predicting the interaction constants. For compositions low in methane, it is apparent that the average error in pressure for the least squares evaluation of the coefficients of the second and third groups shown in Figure 6 is somewhat larger than for the average error in volume shown in Figure 5. The root-mean-square error in the compressibility factor with volume and temperature as the independent variables is shown in Figure 7. The general nature of the deviations is similar to that shown in Figures 5 and 6 for the average errors, as would be expected, since the compressibility factor is directly related to the molal volume.

Figure 8 presents a bar chart showing graphically the variation in the average relative error in volume for the different interaction constants. In the first column, the interaction constants were determined by the methods suggested by Benedict as described in this report, utilizing Equation 4 for B_{015}. The second column used the same interaction coefficients, except that a simple linear average for B_{015} is substituted. In the third column is reported the behavior with interaction constants which involve the interaction functions typified by Equations 4 and 5 and which were established by least squares techniques for the second virial coefficient, A_o, B_o, and C_o. Column 4 utilized Benedict's suggestion for interaction constants for only γ and $a\alpha$, whereas least squares techniques were employed in establishing the interaction constants for both the second and third virial coefficients. In column 5, no interaction constants as such were employed, except those for γ, and the coefficients for the equation for each individual mixture were determined by least squares techniques. As would be expected, there is a marked improvement in the degree of agreement, particularly for the liquid phase, by the use of least squares techniques for determining the interaction functions for this binary system. The marked improvement over the linear interaction function suggested by Benedict and shown in column 2 is evident.

The effect of composition upon the accuracy of description of the experimental data is summarized in Table IV. In this instance the data have been considered on the basis of each experimental mixture in the liquid and in the gas phases. In addition, the over-all behavior has been indicated. The latter data are the same as those presented in the preceding tables and for the reader's convenience they have been summarized in the latter part of Table IV.

It appears that the use of interaction constants established by least squares techniques affords an improved method of describing the volumetric behavior of mixtures for which experimental data are available. Much additional work upon other binary mixtures will be required before it will be possible to predict interaction constants from the nature of the components of the mixtures. In any event it appears that the interaction constants suggested by Benedict for all the coefficients except those of the second virial coefficient are adequate for describing the volumetric behavior of mixtures. No information has been presented in this discussion as to the improvements to be realized by use of empirically evaluated values of γ. However, experience (13, 15) with variations in this exponential coefficient indicates that the improvement would be small.

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NOMENCLATURE

A_0, B_0, C_0, a, b, c, α, γ = coefficients for the Benedict equation of state
exp( ) = exponential function
M = molecular weight
N = number of states represented
$\underline{n}$ = mole fraction
P = pressure, pounds per square inch, absolute
R = universal gas constant, (lb./sq. inch)(cu. foot) per (lb.-mole)(° R.)
T = absolute temperature, ° R.
$\underline{V}$ = molal volume, cubic feet per lb.-mole
Z = compressibility factor
Δ = difference in
∂ = partial differential operator
ϵ = average relative error
Σ = summation operator

Subscripts
e = value of property predicted using Benedict equation of state
i = refers to component i
j = refers to component j
n_i = differentiation at constant n_i
P = pressure as dependent variable
T = differentiation at constant T
$\underline{V}$ = volume as dependent variable

LITERATURE CITED

(1) Beattie, J. A., Stockmayer, W. H., J. Chem. Phys. 10, 473 (1942).
(2) Benedict, M., J. Am. Chem. Soc. 59, 2224 (1937).
(3) Benedict, M., Webb, G. B., Rubin, L. C., Chem. Eng. Progr. 47, 419 (1951).
(4) Ibid., p. 449.
(5) Benedict, M., Webb, G. B., Rubin, L. C., J. Chem. Phys. 8, 334 (1940).
(6) Ibid., 10, 747 (1942).
(7) Benedict, M., Webb, G. B., Rubin, L. C., Friend, L., Chem. Eng. Progr. 47, 571 (1951).
(8) Brough, H. W., Schlinger, W. G., Sage, B. H., Ind. Eng. Chem. 43, 2442 (1951).
(9) Guggenheim, E. A., "Mixtures," Clarendon Press, Oxford, 1952.
(10) Hirschfelder, J. O., Curtiss, C. F., Bird, R. B., "Molecular Theory of Gases and Liquids," Wiley, New York, 1954.
(11) Lewis, G. N., Proc. Am. Acad. Arts Sci. 43, 259 (1907).
(12) Opfell, J. B., Sage, B. H., Ind. Eng. Chem. 48, (1956).
(13) Opfell, J. B., Schlinger, W. G., Sage, B. H., Ibid., 46, 1286 (1954).
(14) Sage, B. H., Reamer, H. H., Olds, R. H., Lacey, W. N., Ibid., 34, 1108 (1942).
(15) Selleck, F. T., Opfell, J. B., Sage, B. H., Ibid., 45, 1350 (1953).
(16) Selleck, F. T., Sage, B. H., Am. Doc. Inst., Washington, D. C., Document 3914 (1953).
(17) Stotler, H. H., Benedict, M., Chem. Eng. Progr. Symposium Series 49, 25 (1953).

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Benedict Equation of State

Application to n-Hexane, n-Heptane, n-Nonane, and n-Decane

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The coefficients for n-hexane and n-heptane, n-nonane, and n-decane were established by statistical methods from experimental data. The equation with these coefficients describes the compressibility factor with a standard error of estimate of 1.8% of the maximum value for liquid and gas phases between 80° and 460° F. and up to 10,000 pounds per square inch. The coefficients are not suitable for calculating vapor pressure nor describing the volumetric behavior in the immediate vicinity of the critical state.

The Benedict equation of state may be used to describe the volumetric behavior of the hydrocarbons of relatively high molecular weight, or to predict the behavior of the liquid or gas phases at pressures as high as 10,000 pounds per square inch, but not to describe their phase behavior.

The Benedict equation of state (4, 5) is a useful empirical relation for interpolating the volumetric and phase behavior of the lighter hydrocarbons. The work of Benedict (4, 5) and coworkers was for the most part limited to a maximum pressure of approximately 4000 pounds per square inch.

In an effort to extend the range of pressures to which the equation may be applied, studies of its effectiveness (11, 15) were made at pressures up to 10,000 pounds per square inch in the temperature interval between -100° and +572° F. for the paraffin hydrocarbons lighter than n-pentane. These studies indicated that the equation could be employed to describe the volumetric behavior of pure hydrocarbons in the liquid and gas phases with reasonable accuracy throughout the greater ranges of pressure and temperature. Sufficient experimental data must be available to permit the equation to be employed as an interpolative rather than an extrapolative device. The error may be large in regions where the relationship of pressure, volume, and temperature established experimentally is not used in the evaluation of the coefficients. Throughout this discussion the term "standard error of estimate" is used as an abbreviation for the phrase "standard error of estimate for the compressibility factor from stated values of the molal volume and temperature."

The coefficients for several of the lighter hydrocarbons as published by Benedict and others (2-6) describe the volumetric behavior of the gas phase and the two-phase pressure of these substances. For mixtures, the thermodynamic properties of the gas phase and the compositions of the co-existing phases in the heterogeneous region were represented with reasonable accuracy (2-6). Conventional least squares techniques (10) with automatic digital computing equipment were employed in

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